ELECTROCHEMICAL OXIDATION OF ORGANIC COMPOUNDS

N. L. WEINBERG AND H. R. WEINBERG*

Central Research Division, American Cyanamid Company, Stamford, Connecticut 06904

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CONTENTS

I. INTRODUCTION

There are a number of reviews available dealing with electroorganic chemistry, including treatments of electrochemical reductions (182, 206, 644), the Kolbe reaction (315, 811, 823), fuel-cell reactions (635), and both brief (88, 782, 783) and detailed (12, 76, 161, 178, 206, 747) discussions of anodic reactions. The present review attempts to bring the review of Fichter (206) up to date with respect to electrochemical oxidation of organic compounds. Anodic halogenation of aromatic compounds, fluorination (85), the Kolbe electrosynthesis, and fuel-cell oxidations are not dealt with here. Recently a series of bibliographies by Swann (747a) have appeared, which are highly recommended for both anodic and cathodic processes.

Electrochemical kinetic studies embodying such methods as polarography, cyclic voltammetry, chronopotentiometry, etc. are presented only to the extent of establishing evidence for a particular mechanism. In a number of cases, relatively stable reactive species (radicals and cationic intermediates) have been discovered with the aid of these techniques and are included in the tables if sufficient additional evidence has been presented for their existence. A table of anodic half-wave potentials ($E_{1/2}$) of a considerable number of organic compounds is given to provide the reader with a convenient reference source, since there is not, at present, any extensive compilation of anodic values available (see Table I).

No claim is made that all the literature has been included on the subject. The tables are arranged in such a manner that oxidations of particular functional groups or classes of compounds may be found. In several cases, however, reactions of a compound A in presence of B may be discovered in one or the other section; thus alkylations of olefinic compounds in the presence of carboxylic acids are listed under Electrolysis (Non-Kolbe) of Carboxylic Acids (section III.I) rather than under Oxidation of Olefinic and Acetylenic Compounds (section III.B). Yields are listed where available. Although often not specified in the tables, these may be in units of weight per cent, mole per cent, or area per cent. In a number of instances the yields have been reported in terms of weight of product per total weight of starting material (g/gsm) in keeping with the preference of the literature. Where several procedures, dif-

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* Presently with Clairol Incorporated, Stamford, Conn.

fering chiefly in the anode material, afforded a large variety of products, all of the products have been listed together and the best yields tabulated.

II. GENERAL PRINCIPLES

Examination of almost any sizable electroorganic review reveals that the general plan of approach has been to treat the variables of the reaction first. Rather than repeat these in detail here, we refer the reader to the reviews of Swann (747), Allen (12), and Eberson (161). The former two works are also useful for their descriptions of electrochemical cells and procedures.

A. CHEMICAL *vs.* ELECTROCHEMICAL OXIDATION

In principle, any successful chemical oxidation should have its electrochemical counterpart. The converse should also be true providing the specific chemical oxidant is known. In practice, however, the two techniques are not parallel at present but appear to be almost entirely complimentary, a situation which will assuredly change as knowledge of the factors influencing chemical and electrochemical oxidation increases.

Once the large number of variables of the electrochemical procedure have been determined, the advantages are generally numerous. These include the following: *convenience in work-up* (there is no chemical oxidant or its products to remove which means that work-up in many cases requires removal of only solvent and electrolyte); *low cost* (neglecting the initial cost of equipment, including items such as stable power supply, potentiostat, voltmeter, ammeter, coulometer, cells, and electrodes, power is relatively inexpensive compared to chemical reagents); and *yield* (often adequate or excellent). In addition, owing to its complimentary nature, unusual reaction products may be obtained from the electrochemical technique. For comparison, the reactions of a number of chemical oxidants have been included in the various discussions.

B. ELECTROCHEMICAL DATA

Far more electrochemical literature exists in the form of half-wave potentials and current–potential relationships than does knowledge of the nature of the products, but these data are necessary for understanding the fundamentals of the process and in general are of considerable value for carrying out controlled-potential electrolyses (cpe) using a third electrode as reference.

Selected values of oxidation potentials are presented in Table I to enable the reader to conveniently interpret the results of section III, especially where cpe is employed. For the sake of brevity, two common solvent systems, acetonitrile (CH_3CN) and acetic acid (HOAc), are referred to as A and B, and reference electrodes are designated as X, Y, and Z for the saturated calomel electrode (sce), $Ag|0.01\ N\ Ag^+$, and $Ag|0.1\ N\ Ag^+$, respectively. Oxidation potentials are given as half-wave potentials ($E_{1/2}$) unless otherwise stated (E_p or $E_{p/2}$ from voltammetry, and $E_{1/4}$ from chronopotentiometry) (141, 299, 592).

C. CONSTANT CURRENT, CONSTANT CELL VOLTAGE, AND CONTROLLED-POTENTIAL ELECTROLYSES

Electrochemical oxidations may be carried out at constant cell voltage, at constant current, or by controlling the potential of the working electrode (12, 143, 490, 491, 537, 659). Of these three general methods controlled-potential electrolysis (cpe) carried out with a potentiostat is by far the most suitable and elegant manner of operation. The potentiostat controls the current through the cell so that the potential of the working electrode is maintained at a preset value against the reference electrode. The optimum setting is predetermined either from polarographic data ($E_{1/2}$ values) or, better, from knowledge of the current-potential relationships of the reactants in the actual solution under study. In addition to the potentiostat setting, however, there are a number of operating conditions governing a cpe which may be described by Eq I–III for electrode processes controlled by the rate of mass transport to the electrode, where i_t is the instantaneous current, i_i is the initial current, k is a constant, V is the solution volume (ml), C_i is the initial concentration of reactant (mole cm^{-3}), A is the area of the anode (cm^2), t is the time (min), D is the diffusion coefficient (cm^2 sec^{-1}), and δ is the Nernst diffusion layer thickness.

$$i_t = i_i 10^{-kt} \qquad \text{(I)}$$

$$k = 0.43\,\frac{DA}{V\delta} \qquad \text{(II)}$$

$$\frac{C_i}{C_t} = \frac{i_i}{i_t} \qquad \text{(III)}$$

Equations I and II signify that a short electrolysis time is achieved by a large anode surface area, a small solution volume, and a small diffusion layer thickness (attained by efficient stirring and an increase in temperature). An increase in temperature also lowers the solution viscosity and increases the value of the diffusion coefficient, again increasing the reaction rate. The electrolysis time needed to complete the reaction is independent of the reactant concentration, since k is independent of concentration. Equation III allows calculation of the amount of remaining reactant as the current decreases with time. By plotting log i_t against time, a straight line is frequently obtained obeying Eq IV. Now since Faraday's law may be written as (V),

$$\log i_t = \log i_i - kt \qquad \text{(IV)}$$

$$Q = \int_0^\infty i dt = nFN^0 \qquad \text{(V)}$$

where Q is the quantity of electricity (coulombs), n is the total number of electrons per molecule involved in the over-all reaction, F is 96,500 coulombs, and N^0 is the number of moles of the substance initially, then from Eq I

$$Q = i_l/2.303k \tag{VI}$$

and with knowledge of i_l and k the value of n may be determined (537).

A large variety of anodic oxidation reactions have been carried out by cpe techniques and in many cases improvements in yield and purity of products have been observed in comparison to classical methods of electrolysis at constant current or voltage. But there still remain many areas in which the latter methods have been used with success.

III. OXIDATION REACTIONS

A. OXIDATION OF AROMATIC COMPOUNDS (TABLE II)

To simplify the presentation, the material, here and in many of the sections to follow, is considered from the mechanistic standpoint of the aromatic ring undergoing electron transfer at the anode to give rise to cationic species. The latter may subsequently react with solvent or otherwise. It must be emphasized, however, that relatively little is known about many of the oxidation processes other than the products so that the arrangement of sections should not be considered to imply the actual mode of reaction.

1. *Hydroxylation–Oxidation*
(*ArX:* X = *H, Alkyl, Alkoxyl, Nitro, Cyano*)

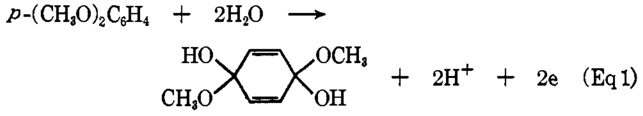
Table II lists electrooxidations of aromatic compounds in aqueous media. Examination of Table I readily demonstrates that many of the aromatics tabulated are oxidized at significantly higher anodic potentials than the aqueous media. No practical yield of product should then be obtained if the mechanism of reaction entails discharge of the aromatic as the primary oxidation step. Indeed toluene is almost unoxidizable in alcoholic H_2SO_4 solution, the products being due chiefly to solvent oxidation (472). In contrast, toluene is completely degraded to carbon dioxide and water in aqueous H_2SO_4, while a reasonable yield of product is achieved in aqueous acetone–H_2SO_4 solution (548).

It was recognized early that oxidations in aqueous media may occur by reaction of the substrate with anodically generated atomic oxygen, hydroxy radicals, or peroxide species (76, 261, 473, 626). A large body of evidence has since accumulated to support the involvement of anode surface oxides in a variety of organic reactions (60, 63, 126, 281, 792). It has been shown (281) that Pt in aqueous solution is free of oxygen or oxides below about 0.9 V (reversible hydrogen electrode). In this region certain unsaturated hydrocarbons and alcohols may be oxidized. The electrode becomes nearly "passive" for the oxidation of many of these compounds near 0.9 V while, with increasing potential to 1.8 V, the Pt surface is progressively oxidized until oxygen evolution occurs. Above 1.8 V ozone evolution commences. Surface oxides such as $Pt(OH)_2$, PtO_2, $PtO_2(O_2)$, and PtO have been formulated. Oxidation of the organic material proceeds by chemical reaction with the oxide species (or even through the oxide layer, the layer rather than the metal surface acting as the inert electrode) (127).

Characteristically, many of the oxidations in aqueous media afford a multitude of products, a situation which could be remedied to some extent by use of a suitable diaphragm to separate anode and cathode compartments. But this measure does not limit the oxidation of primary products (usually alcohols and phenols), and relatively difficult to oxidize intermediates such as quinones may be further degraded to maleic acid, etc. (410, 863). Successful results have been observed in a number of cases, however, by careful control of a large number of variables and with addition of suitable "oxygen" carriers. Electrooxidation of aromatics in aqueous media still remains more of an art than a science.

A recent study (395) of oxidation of aryl-activated methylene groups has demonstrated that little or no oxidation ensues in acid or buffered alkaline media at smooth Pt electrodes. When the concentration of base was increased to an optimum value (0.4–0.5 N), α-hydroxylated product could be obtained along with the corresponding ketone and some t-butyl ether (the solvent consisted of t-butyl alcohol and water). The effect of increasing pH and the lack of chemical reaction under similar conditions with molecular oxygen, t-butyl hydroperoxide, and di-t-butyl peroxide suggests a free-radical mechanism involving hydroxy radicals.

There are several reactions which apparently proceed by initial charge transfer of the aromatic followed by reaction with water. The aromatic ethers and the polycyclic aromatic hydrocarbons are probably among this group. Thus the oxidation of hydroquinone dimethyl ether to benzoquinone may follow a mechanism whereby an over-all loss of two electrons (simultaneous or stepwise) may occur followed by reaction of the cationic species (cation radical or dication) with water to form an unstable dihemiacetal of hydroquinone. The latter would readily decompose to benzoquinone and CH_3OH (Eq 1).



p-$(CH_3O)_2C_6H_4 + 2H_2O \longrightarrow$ $+ 2H^+ + 2e$ (Eq 1)

TABLE I
OXIDATION POTENTIALS (Volts) OF ORGANIC COMPOUNDS

Solvent systems

A (CH_3CN, perchlorate salt such as $LiClO_4$, $NaClO_4$, $(C_2H_5)_4NClO_4$, $(n\text{-}C_3H_7)_4NClO_4$, $(n\text{-}C_4H_9)_4NClO_4$)
B (HOAc, NaOAc, or KOAc)

References electrodes: X, sce; Y, Ag|0.01 N Ag^+; Z, Ag|0.1 N Ag^+

(a) Aromatic Compounds
Hydrocarbons

Compound	Solvent system	Anode	$E_{1/2}$	Ref electrode	Ref
Benzene	A	Pt	2.08,	Z	503
Toluene	A	Pt	1.98	Z	503
o-Xylene	A	Pt	1.58, 2.04[a]	Z	503
m-Xylene	A	Pt	1.58	Z	582
p-Xylene	A	Pt	1.56	Z	582
Mesitylene	A	Pt	1.55	Z	581
	B	Pt	1.90	X	167
1,2,3-Trimethylbenzene	A	Pt	1.58	Z	581
1,2,4-Trimethylbenzene	A	Pt	1.41	Z	581
1,2,3,5-Tetramethylbenzene	A	Pt	1.50, 199[a]	Z	503
1,2,4,5-Tetramethylbenzene	A	Pt	1.29	Z	581
Pentamethylbenzene	A	Pt	1.28	Z	581
	B	Pt	1.62	X	167
Hexamethylbenzene	A	Pt	1.16	Z	581
	B	Pt	1.52	X	167
Naphthalene	A	Pt	1.34	Z	503
	B	Pt	1.72	X	167
1-Methylnaphthalene	A	Pt	1.24	Z	503
	B	Pt	1.53	X	167
2-Methylnaphthalene	A	Pt	1.22	Z	503
	B	Pt	1.55	X	167
2,3-Dimethylnaphthalene	A	Pt	1.08, 1.34[a]	Z	503
Biphenyl	A	Pt	1.48	Z	511
	B	Pt	1.91	X	167
Indan	A	Pt	1.59, 2.02[a]	Z	511
Indene	A	Pt	1.23	Z	511
Anthracene	A	Pt	0.84	Z	511
	B	Pt	1.20	X	167
9,10-Dimethylanthracene	A	Pt	0.65	Z	511
9,10-Diphenylanthracene	A	Pt	0.92	Y	621
Acenaphthene	A	Pt	0.95	Z	503
	B	Pt	1.36	X	167
Fluorene	A	Pt	1.25	Z	511
	B	Pt	1.65	X	167
Phenanthrene	A	Pt	1.23	Z	511
	B	Pt	1.68	X	167
Tetracene	A	Pt	0.54, 1.20[a]	Z	511
Azulene	A	Pt	0.71	X	650
Rubrene	*m*	Pt	0.82	X	632
1,4,5,8-Tetraphenylnaphthalene	A	Pt	1.39	X	894
9,10-Bis(phenylethynyl)anthracene	A	Pt	1.17	X	894
1,2-Benzanthracene	A	Pt	1.00, 1.09[a]	Y	621
Pyrene	A	Pt	1.06, 1.24[a]	Y	621
Chrysene	A	Pt	1.22, 1.27[a]	Y	621
Triphenylene	A	*Pt*	1.46, 1.55[a]	Y	621
1,2,5,6-Dibenzanthracene	A	Pt	1.00, 1.26[a]	Z	511
Benzo[*a*]pyrene	A	Pt	0.76	Z	511
Coronene	A	Pt	1.23	X	650

Ethers, Thioethers, and Acetates

Compound	Solvent system	Anode	$E_{1/2}$	Ref electrode	Ref
Anisole	A	Pt	1.76	X	889
1,2-Dimethoxybenzene	A	Pt	1.45	X	889
1,4-Dimethoxybenzene	A	Pt	1.34	X	889
1,2,3-Trimethoxybenzene	A	Pt	1.42	X	889
1,2,4-Trimethoxybenzene	A	Pt	1.12	X	889
1,3,5-Trimethoxybenzene	A	Pt	1.49	X	889
1,2,3,4-Tetramethoxybenzene	A	Pt	1.25	X	889
Pentamethoxybenzene	A	Pt	1.07	X	889
Hexamethoxybenzene	A	Pt	1.24	X	889
1-Methoxynaphthalene	A	Pt	1.38	X	894
2-Methoxynaphthalene	A	Pt	1.52	X	894
1,3-Dimethoxynaphthalene	A	Pt	1.27	X	894

Table I (*Continued*)

Compound	Solvent system	Anode	$E_{1/2}$	Ref electrode	Ref
1,4-Dimethoxynaphthalene	A	Pt	1.10	X	894
1,5-Dimethoxynaphthalene	A	Pt	1.28	X	894
1,6-Dimethoxynaphthalene	A	Pt	1.28	X	894
1,7-Dimethoxynaphthalene	A	Pt	1.28	X	894
1,8-Dimethoxynaphthalene	A	Pt	1.17	X	894
2,3-Dimethoxynaphthalene	A	Pt	1.39	X	894
2,6-Dimethoxynaphthalene	A	Pt	1.33	X	894
2,7-Dimethoxynaphthalene	A	Pt	1.47	X	894
1,4,5,8-Tetramethoxynaphthalene	A	Pt	0.70	X	894
1,5-Dimethoxy-4,8-diphenoxynaphthalene	A	Pt	0.98	X	894
9-Methoxyanthracene	A	Pt	1.05	X	894
9,10-Dimethoxyanthracene	A	Pt	0.98	X	894
9,10-Bis(2,6-dimethoxyphenyl)anthracene	A	Pt	1.18	X	894
9,10-Diphenoxyanthracene	A	Pt	1.20	X	894
4-Methoxybiphenyl	A	Pt	1.53	X	894
4,4'-Dimethoxybiphenyl	A	Pt	1.30	X	894
3,3'-Dimethoxybiphenyl	A	Pt	1.60	X	894
2,2'-Dimethoxybiphenyl	A	Pt	1.51	X	894
10,10'-Dimethoxy-9,9'-bianthracenyl	A	Pt	1.10	X	894
1,6-Dimethoxypyrene	A	Pt	0.82	X	894
Thioanisole	A	Pt	1.56	X	892
p-Bis(methylthio)benzene	A	Pt	1.19	X	892
m-Bis(methylthio)benzene	A	Pt	1.45	X	892
o-Bis(methylthio)benzene	A	Pt	1.35	X	892
1,3,5-Tris(methylthio)benzene	A	Pt	1.43	X	892
1,2,4,5-Tetrakis(methylthio)benzene	A	Pt	1.08	X	892
p-Methylthioanisole	A	Pt	1.22	X	892
m-Methylthioanisole	A	Pt	1.45	X	892
o-Methylthioanisole	A	Pt	1.35	X	892
1-(Methylthio)naphthalene	A	Pt	1.32	X	894
2-(Methylthio)naphthalene	A	Pt	1.37	X	894
1,4-Bis(methylthio)naphthalene	A	Pt	1.07	X	894
1,5-Bis(methylthio)naphthalene	A	Pt	1.27	X	894
1,8-Bis(methylthio)naphthalene	A	Pt	1.09	X	894
2,3-Bis(methylthio)naphthalene	A	Pt	1.36	X	894
2,6-Bis(methylthio)naphthalene	A	Pt	1.10	X	894
2,7-Bis(methylthio)naphthalene	A	Pt	1.33	X	894
1,5-Dimethoxy-4,8-bis(methylthio)naphthalene	A	Pt	0.70	X	894
9,10-Bis(methylthio)anthracene	A	Pt	1.11	X	894
4,4'-Bis(methylthio)biphenyl	A	Pt	1.26	X	894
3,3'-Bis(methylthio)biphenyl	A	Pt	1.48	X	894
2,2'-Bis(methylthio)biphenyl	A	Pt	1.39	X	894
1,6-Bis(methylthio)pyrene	A	Pt	0.96	X	894
Phenyl acetate	B	Pt	1.30	X	167
p-Acetoxyanisole	B	Pt	1.12	X	167
m-Acetoxyanisole	B	Pt	1.25	X	167
o-Acetoxyanisole	B	Pt	1.74	X	167
1,2-Diacetoxybenzene	B	Pt	Near 2.5	X	167
1,3-Diacetoxybenzene	B	Pt	1.46	X	167
1,4-Diacetoxybenzene	B	Pt	Near 2.5	X	167
1-Acetoxynaphthalene	B	Pt	1.67	X	167
2-Acetoxynaphthalene	B	Pt	1.86	X	167
2-Acetoxybiphenyl	B	Pt	2.04	X	167
4-Acetoxybiphenyl	B	Pt	1.90	X	167
Heterocyclic Compounds (O, S)					
Furan	B	Pt	1.70	X	167
2,5-Dimethylfuran	B	Pt	1.20	X	167
Thiophene	A	Pt	1.60	Z	503
	B	Pt	1.91	X	167
Diphenylene dioxide	A	Pt	0.991	Y	35
1,3,4,7-Tetraphenylisobenzofuran	*d*	Pt	0.98	Z	895
Phenoxathiin	A	Pt	0.825, 1.32[a]	Y	35
Thianthrene	A	Pt	0.865, 1.19[a]	Y	35, 890
Naphthalene 1,8-disulfide	A	Pt	0.95	X	890
Nitro Aromatics					
1-Nitronaphthalene	A	Pt	1.62	Z	511
9-Nitroanthracene	A	Pt	1.25	Z	511
(b) Olefinic Compounds					
2-Methyl-1-butene	A	Pt	1.97	Z	582
Cyclohexene	A	Pt	1.89	Z	582

TABLE I (*Continued*)

Compound	Solvent system	Anode	$E_{1/2}$	Ref electrode	Ref
1,1-Diphenylethylene	B	Pt	1.52	X	167
trans-Stilbene	B	Pt	1.51	X	167
3,4-Dimethoxypropenylbenzene	A	Pt	0.98, 1.2,^{a} 1.4^b	X	595
	A^c	Pt	1.08	X	595
Tetrakis(dimethylamino)ethylene	A	Hg	−0.75, −0.61^a	X	461
1,4-Cyclohexadiene	A	Pt	1.6	Y	306
1,3-Butadiene	A	Pt	2.03	Z	581
2-Methyl-1,3-butadiene	A	Pt	1.84	Z	581
2,3-Dimethyl-1,3-butadiene	A	Pt	1.83	Z	581
1-Pyrrolidino-4-cyano-4-phenyl-1,3-butadiene	*d*	Pt	0.22	*v*	304
1-Piperidino-4-cyano-4-phenyl-1,3-butadiene	*d*	Pt	0.155	*v*	304
1-Morpholino-4-cyano-4-phenyl-1,3-butadiene	*d*	Pt	0.19	*v*	304
1-Piperidino-4,4-dicarbethoxy-1,3-butadiene	*d*	Pt	0.38	*v*	304
Tropilidene	A	Pt	1.13	Y	306
Bis-2,4,6-cycloheptatrien-1-yl	A	Pt	1.03	Y	306
Cyclooctatetraene	B	Pt	1.42	X	167
	(c) Amines				
	Aliphatic Amines				
n-Propylamine	A	Pt	1.63 E_p	*n*	516
n-Butylamine	A	Pt	1.63 E_p	*n*	516
Isobutylamine	A	Pt	1.62 E_p	*n*	516
t-Butylamine	A	Pt	1.64 E_p	*n*	516
n-Pentylamine	A	Pt	1.69 E_p	*n*	516
n-Nonylamine	A	Pt	1.72 E_p	*n*	516
Diethylamine	A	Pt	1.89	Z	503
Dipropylamine	A	Pt	1.26 E_p	*n*	516
Di-*n*-butylamine	A	Pt	1.31 E_p	*n*	516
Di-*sec*-butylamine	A	Pt	1.40 E_p	*n*	516
Di-*n*-pentylamine	A	Pt	1.35 E_p	*n*	516
Dibenzylamine	A	Pt	1.49 E_p	*n*	516
Trimethylamine	A	Pt	1.29 E_p	*n*	516
Triethylamine	A	Pt	1.19 E_p	*n*	516
Tripropylamine	A	Pt	1.02 E_p	*n*	516
Tri-*n*-butylamine	A	Pt	1.02 E_p	*n*	516
Dimethylaminoacetonitrile	A	Pt	1.59 E_p	*n*	516
Tribenzylamine	A	Pt	1.27 E_p	*n*	516
Tripentylamine	A	Pt	1.13 E_p	*n*	516
	Aromatic Amines				
Aniline	A	Pt	0.70	Z	611
	A	Pt	0.54	Z	820
p-Toluidine	*o*	Graphite	0.780	X	501
	j	Graphite	0.537	X	744
m-Toluidine	*o*	Graphite	0.829	X	501
	j	Graphite	0.606	X	744
o-Toluidine	*o*	Graphite	0.494	X	501
	j	Graphite	0.595	X	744
p-Nitroaniline	A	Pt	0.97, 1.14^a	Z	820
	j	Graphite	0.935	X	744
m-Nitroaniline	A	Pt	0.90	Z	820
	j	Graphite	0.854	X	744
o-Nitroaniline	A	Pt	1.07	Z	820
	j	Graphite	0.989	X	744
p-Bromoaniline	A	Pt	0.61	Z	820
m-Bromoaniline	A	Pt	0.70	Z	820
p-Chloroaniline	A	Pt	0.60	Z	820
	j	Graphite	0.675	X	744
m-Chloroaniline	*j*	Graphite	0.774	X	744
o-Chloroaniline	*j*	Graphite	0.742	X	744
p-Anisidine	A	Pt	0.26	Z	820
	j	Graphite	0.393	X	744
m-Anisidine	*j*	Pt	0.615	X	744
o-Anisidine	A	Pt	0.34	Z	820
	j	Graphite	0.498	X	744
2,4-Dinitroaniline	A	Pt	1.48	Z	820
2,4-Dichloroaniline	A	Pt	0.78	Z	820
1,3,5-Trichloroaniline	A	Pt	0.95	Z	820
p-Aminoacetophenone	*j*	Graphite	0.820	X	744
m-Aminoacetophenone	*j*	Graphite	0.758	X	744
o-Aminoacetophenone	*j*	Graphite	0.847	X	744
2,4,6-Tri-*t*-butylaniline	A	Pt	0.530	Y	93

TABLE I (*Continued*)

Compound	Solvent system	Anode	$E_{1/2}$	Ref electrode	Ref
p-Amino-N,N-dialkylanilines[d']					44
p-Phenylenediamine	*o*	Graphite	0.495	X	501
m-Phenylenediamine	*o*	Graphite	0.811	X	501
o-Phenylenediamine	*o*	Graphite	0.494	X	501
1-Naphthylamine	A	Pt	0.44	Z	611
2-Naphthylamine	A	Pt	0.54	Z	611
1-Aminoanthracene	A	Pt	0.31	Z	611
2-Aminoanthracene	A	Pt	0.33	Z	611
9-Aminoanthracene	A	Pt	0.15	Z	611
2-Aminophenanthrene	A	Pt	0.59	Z	611
9-Aminophenanthrene	A	Pt	0.46	Z	611
1-Aminopyrene	A	Pt	0.32	Z	611
2-Aminopyrene	A	Pt	0.57	Z	611
6-Aminopyrene	A	Pt	0.38	Z	611
2-Aminobiphenyl	A	Pt	0.65	Z	611
4-Aminobiphenyl	A	Pt	0.55	Z	611
9-Amino-10-phenylanthracene	A	Pt	0.170, 1.020[a]	Y	90
N-Methylaniline	*t*	C paste	0.7 $E_{p/2}$	X	297
Diphenylamine	A	Pt	0.83	X	160
Di-4-tolylamine	A	Pt	0.71, 1.54[a]	X	160
9-Phenylaminoanthracene	A	Pt	0.420	Y	91
9-*p*-Tolylaminoanthracene	A	Pt	0.390	Y	91
9-*p*-Anisylaminoanthracene	A	Pt	0.330	Y	91
9-*p*-Dimethylaminophenylaminoanthracene	A	Pt	−0.074	Y	91
9-*p*-Carbomethoxyphenylaminoanthracene	A	Pt	0.510	Y	91
9-*p*-Nitrophenylaminoanthracene	A	Pt	0.615	Y	91
9-Phenylamino-10-phenylanthracene	A	Pt	0.460, 0.780[a]	Y	91
9-*p*-Tolylamino-10-phenylanthracene	A	Pt	0.420, 0.760[a]	Y	91
9-*p*-Anisylamino-10-phenylanthracene	A	Pt	0.370, 0.745[a]	Y	91
9-*m*-Anisylamino-10-phenylanthracene	A	Pt	0.465, 0.755[a]	Y	91
9-*p*-Dimethylaminophenylamino-10-phenylanthracene	A	Pt	−0.075, 0.600[a]	Y	91
N,N-Dimethylaniline	A	Pt	0.71 $E_{p/2}$	X	708
N,N-Dimethyl-*p*-chloroaniline	A	Pt	0.84 $E_{p/2}$	X	708
N,N-Dimethyl-*p*-nitroaniline	A	Pt	1.19 $E_{p/2}$	X	708
N,N-Dimethyl-*p*-anisylamine	A	Pt	0.49 $E_{p/2}$	X	708
N,N-Dimethyl-*p*-tolylamine	A	Pt	0.65 $E_p/_2$	X	708
N,N-Dimethyl-*p*-anisidine	A	Pt	0.33	Y	891
N,N-Dimethyl-*m*-anisidine	A	Pt	0.49	Y	891
N,N-Dimethyl-*o*-anisidine	A	Pt	0.48	Y	891
3,4-Dimethoxy-N,N-dimethylaniline	A	Pt	0.20	Y	891
3,5-Dimethoxy-N,N-dimethylaniline	A	Pt	0.50	Y	891
2,4-Dimethoxy-N,N-dimethylaniline	A	Pt	0.27	Y	891
N,N-Diethylaniline	A	Pt	0.34	Z	820
N,N-Diethyl-*p*-chloroaniline	A	Pt	0.47	Z	820
N-Methyldiphenylamine	A	Pt	0.84 $E_{p/2}$	X	708
N-Methyl-di-*p*-tolylamine	A	Pt	0.60 $E_{p/2}$	X	708
N-Methyl-di-*p*-anisylamine	A	Pt	0.65 $E_{p/2}$	X	708
N-Methyl-N-phenyl-*p*-anisylamine	A	Pt	0.77 $E_{p/2}$	X	708
N,N,N',N'-Tetramethyl-*p*-phenylenediamine	A	Pt	−0.10	Y	891
N,N,N',N'-Tetramethyl-*m*-phenylenediamine	A	Pt	0.32	Y	891
N,N,N',N'-Tetramethyl-*o*-phenylenediamine	A	Pt	0.28	Y	891
Triphenylamine	A	Pt	0.92 $E_{p/2}$	X	708
Tri-*p*-anisylamine	A	Pt	0.52 $E_{p/2}$	X	708
Tri-*p*-tolylamine	A	Pt	0.75 $E_{p/2}$	X	708
Tri-*p*-chlorophenylamine	A	Pt	1.04 $E_{p/2}$	X	708
Tri-*p*-bromophenylamine	A	Pt	1.05 $E_{p/2}$	X	708
N,N-Di(*p*-anisyl)aniline	A	Pt	0.63 $E_{p/2}$	X	708
N,N-Diphenyl-*p*-anisylamine	A	Pt	0.76 $E_{p/2}$	X	708
N,N-Di(*p*-nitrophenyl)aniline	A	Pt	1.34 $E_{p/2}$	X	708
N,N-Diphenyl-*p*-nitroaniline	A	Pt	1.15 $E_{p/2}$	X	708
N,N,N',N'-Tetramethylbenzidine	A	Pt	0.43	X	894
1-Dimethylaminonaphthalene	A	Pt	0.75	X	894
2-Dimethylaminonaphthalene	A	Pt	0.67	X	894
Heterocyclic Amines					
Pyrrole	A	Pt	0.76	Z	503
Pyridine	A	Pt	1.82	Z	503
5,10-Dihydro-5,10-dimethylphenazine	A	Pt	0.11, 0.83[a] $E_{p/2}$	X	584
5,10-Dihydro-5-methyl-10-phenylphenazine	A	Pt	0.13, 0.87[a] $E_{p/2}$	X	584
5,10-Dihydro-5,10-diphenylphenazine	A	Pt	0.20, 0.94[a] $E_{p/2}$	X	584
Indole alkaloids[e']					13
Phenothiazine	A	Pt	0.27, 0.77[a]	Y	49, 51

TABLE I (*Continued*)

Compound	Solvent system	Anode	$E_{1/2}$	Ref electrode	Ref
N-Methylphenothiazine	A	Pt	0.40, 0.97^a	Y	51
Chloropromazine hydrochloride	*p*	Pt	0.6	X	545
	q	Pt	0.37, 0.95^a	X	545
10-[3-(4-β-Hydroxyethyl-1-piperazinyl)propyl]-2-chlorophenothiazine	*r*	Pt	0.550	*s*	397
Persantine	A	Pt	0.22, 0.47^a	Y	24
	Triphenylmethane Dyes				
Crystal violet	*p*	Pt	0.632, 0.886^a $E_{p/2}$	X	298
Malachite green	*p*	Pt	0.690 $E_{p/2}$	X	298
p,p'-Methylenebis(N,N-dimethylaniline)	*p*	Pt	0.775 $E_{p/2}$	X	298
Ethyl violet	*p*	Pt	0.796, 0.954^a $E_{p/2}$	X	298
Brilliant green	*p*	Pt	0.798 $E_{p/2}$	X	298
	(d) Phenols and Aminophenols				
Phenol	A	Pt	1.04	Z	611
p-Cresol	*j*	Graphite	0.543	X	744
m-Cresol	*j*	Graphite	0.607	X	744
o-Cresol	*j*	Graphite	0.556	X	744
p-Methoxyphenol	*j*	Graphite	0.406	X	744
m-Methoxyphenol	*j*	Graphite	0.619	X	744
o-Methoxyphenol	*j*	Graphite	0.456	X	744
p-Nitrophenol	*j*	Graphite	0.924	X	744
m-Nitrophenol	*j*	Graphite	0.855	X	744
o-Nitrophenol	*j*	Graphite	0.846	X	744
p-Hydroxyacetophenone	*j*	Graphite	0.791	X	744
m-Hydroxyacetophenone	*j*	Graphite	0.754	X	744
o-Hydroxyacetophenone	*j*	Graphite	0.801	X	744
p-Chlorophenol	*j*	Graphite	0.653	X	744
m-Chlorophenol	*j*	Graphite	0.734	X	744
o-Chlorophenol	*j*	Graphite	0.625	X	744
p-*t*-Butylphenol	*j*	Graphite	0.578	X	744
o-*t*-Butylphenol	*j*	Graphite	0.552	X	744
p-Phenylphenol	*j*	Graphite	0.534	X	744
2,6-Di-*t*-butyl-*p*-cresol	A	Pt	0.93, 2.06	Z	503
Hydroquinone	*j*	Graphite	0.234	*f*	181
Resorcinol	*j*	Graphite	0.613	*f*	181
Catechol	*j*	Graphite	0.349	*f*	181
1-Naphthol	A	Pt	0.74	Z	611
2-Naphthol	A	Pt	0.82	Z	611
9-Anthranol	A	Pt	0.44	Z	611
2-Hydroxybiphenyl	A	Pt	0.97	Z	611
4-Hydroxybiphenyl	A	Pt	0.89	Z	611
4-Phenyl-2-chlorophenol	*k*	Pt	0.56	X	720
2,4-Dichlorophenol	*k*	Pt	0.66	X	720
2-Chloro-4-bromophenol	*k*	Pt	0.67	X	720
4-Carbomethoxy-2-chlorophenol	*k*	Pt	0.87	X	720
4-Carboxy-2-chlorophenol	*k*	Pt	0.92	X	720
4-Phenyl-2,6-dicyanophenol	*l*	Graphite	>0.800	*f*	740
2,4,6-Triphenyl-3,5-dicyanophenol	*l*	Graphite	0.723	*f*	740
	B	Graphite	1.061	*f*	740
2,4,6-Triphenyl-3-cyanophenol	*l*	Graphite	0.433	*f*	740
	B	Graphite	0.926	*f*	740
2,3,4,5,6-Pentaphenylphenol	*l*	Graphite	0.366	*f*	740
	B	Graphite	0.930	*f*	740
3-Chloro-2,4,6-triphenylphenol	*l*	Graphite	0.347	*f*	740
	B	Graphite	0.858	*f*	740
2,3,4,6-Tetraphenylphenol	*l*	Graphite	0.238	*f*	740
	B	Graphite	0.854	*f*	740
2,4,6-Tris(biphenyl-4-)phenol	*l*	Graphite	0.216	*f*	740
2,4,6-Triphenylphenol	*l*	Graphite	0.211	*f*	740
	B	Graphite	0.786	*f*	740
2,4,6-Tris(*p*-methoxyphenyl)phenol	*l*	Graphite	0.124	*f*	740
	B	Graphite	0.671	*f*	740
4-*t*-Butyl-2,6-diphenylphenol	*l*	Graphite	0.120	*f*	740
6-*t*-Butyl-2,4-diphenylphenol	*l*	Graphite	0.112	*f*	740
4,6-Di-*t*-butyl-2-phenylphenol	*l*	Graphite	0.76	*f*	740
2,6-Di-*t*-butyl-4-phenylphenol	*l*	Graphite	−0.14	*f*	740
2,4,6-Tri-*t*-butylphenol	*l*	Graphite	−0.59	*f*	740
4-Carboxy-2,6-di-*t*-butylphenol	A	Pt	1.68	X	808
4-Hydroxymethyl-2,6-di-*t*-butylphenol	A	Pt	1.72	X	808
Vanillate anion	A	Pt	0.22, 0.53^a	X	808

TABLE I (*Continued*)

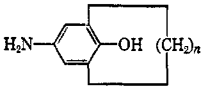
Compound	Solvent system		$E_{1/2}$	Ref electrode	Ref
2,4,6,7-Tetramethyl-5-hydroxycoumarin	*f'*	Hg	0.219	X	727
2,2,4,6,7-Pentamethyl-5-hydroxycoumarin	*f'*	Hg	0.219	X	727
p-Aminophenol	*u*	Pt	0.124	X	396
Adrenaline	*g*	C paste	0.7 E_p	X	341
2,6-Di-*t*-butyl-4-aminophenol	A	Pt	0.190, 1.800[a]	Y	93
 *n* = 9–19, in aqueous solution at Hg					645
p-Azophenol	*g'*	Hg	0.17	X	469
(e) Enolates, Enediols, Nitroalkanes					
Sodium 4,4-dicarbethoxybutadien-1,3-olate	*d*	Pt	0.17	*v*	304
Sodium 4-cyano-4-carboxamidobutadien-1,3-olate	*d*	Pt	−0.05	*v*	304
2,2'-Pyridoin	*u*	Hg	−0.21	X	359
Ascorbic acid, dihydroxyacrylic acid, dihydroxyfumaric acid, coumarindiol[i]					74, 282, 804, 836
Nitroethane	*w*	Hg	Near 0.8	X	855
Dinitroethane	*w*	Hg	Near 0.4	X	855
(f) Amides					
Acetamide	A	Pt	Near 2.0 E_p	X	596
N-Methylacetamide	A	Pt	1.81 E_p	X	596
N,N-Dimethylacetamide	A	Pt	1.32 E_p	X	596
N,N-Dimethylformamide	B	Pt	1.90	X	167
Thiourea	*g*	Hg	−0.90	X	398
Thiobenzamide	*h'*	Hg	−0.52	X	509
(g) Aliphatic and Aromatic Halides					
Methyl iodide	A	Pt	2.12	Y	551
Neopentyl iodide	A	Pt	2.14	Y	551
Isopropyl iodide	A	Pt	2.04	Y	551
t-Butyl iodide	A	Pt	1.87	Y	551
Chlorobenzene	A	Pt	2.07	Z	582
Bromobenzene	A	Pt	1.98	Z	582
Iodobenzene	A	Pt	1.77	Z	582
p-Chlorotoluene	A	Pt	1.76	Z	582
p-Bromotoluene	A	Pt	1.72	Z	582
1-Bromonaphthalene	A	Pt	1.55	Z	611
2-Bromonaphthalene	A	Pt	1.60	Z	611
4-Bromobiphenyl	A	Pt	1.65	Z	611
9,10-Dibromoanthracene	A	Pt	1.15, 1.47[a]	Z	511
(h) Organometallic Compounds					
Ferrocene	A	Pt	0.307 $E_{1/4}$	X	459
Ruthenocene	A	Pt	0.693 $E_{1/4}$	X	459
Osmocene	A	Pt	0.633, 1.50[a] $E_{1/4}$	X	459
1,1'-Diethylferrocene	A	Pt	0.194 $E_{1/4}$	X	459
Ethylferrocene	A	Pt	0.245 $E_{1/4}$	X	459
Vinylferrocene	A	Pt	0.325 $E_{1/4}$	X	459
Ferrocenecarboxylic acid	A	Pt	0.550 $E_{1/4}$	X	459
Ferrocene phenyl ketone	A	Pt	0.571 $E_{1/4}$	X	459
Acetylferrocene	A	Pt	0.573 $E_{1/4}$	X	459
1,1'-Diacetylferrocene	A	Pt	0.796 $E_{1/4}$	X	459
o-, *m*-, and *p*-Aryl-substituted ferrocenes[h']					496
Sodium tetraphenylborate	*e*	Pyrolytic graphite	0.216 $E_{p/2}$	X	789
Diphenylborinic acid	*e*	Pyrolytic graphite	0.54 $E_{p/2}$	X	789
Dimethylmagnesium	*x*	Hg	−1.2	*y*	647
(i) Carboxylic acids					
2-Biphenylcarboxylic acid	B	Pt	1.71	X	167
Anthranilic acid	*j*	Graphite	0.676	X	744
m-Aminobenzoic acid	*j*	Graphite	0.668	X	744
Salicylic acid	*j*	Graphite	0.845	X	744

TABLE I (*Continued*)

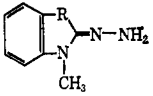
Compound	Solvent system		$E_{1/2}$	Ref electrode	Ref
	(j) Miscellaneous Alcohols				
Allyl alcohol	A	Pt	>2.0	Z	510
Cyclohexanol	A	Pt	>2.0	Z	510
p-Methoxybenzyl alcohol	A	Pt	1.22, 1.64^a	Z	510
m-Methoxybenzyl alcohol	A	Pt	1.28	Z	510
o-Methoxybenzyl alcohol	A	Pt	1.25	Z	510
p-Chlorobenzyl alcohol	A	Pt	1.79	Z	510
m-Chlorobenzyl alcohol	A	Pt	1.85	Z	510
o-Chlorobenzyl alcohol	A	Pt	1.84	Z	510
p-Bromobenzyl alcohol	A	Pt	1.75	Z	510
p-Iodobenzyl alcohol	A	Pt	1.58, 1.91^a	Z	510
p-Methylbenzyl alcohol	A	Pt	1.59	Z	510
Furfuryl alcohol	A	Pt	1.33, 1.82^a	Z	510
Cinnamyl alcohol	A	Pt	1.36, 1.77^a	Z	510
p-Nitrocinnamyl alcohol	A	Pt	1.72	Z	510
Fluorenol	A	Pt	1.31	Z	510
4-Methoxybenzylhydrol	A	Pt	1.23	Z	510
4,4′-Dimethoxybenzylhydrol	A	Pt	1.22	Z	510
4,4’-Dichlorobenzyhydrol	A	Pt	1.77	Z	510
Benzhydrol	A	Pt	>2.0	Z	510
Benzyl alcohol	A	Pt	>2.0	Z	510
p-Bromophenylethylene glycol	A	Pt	1.62	Z	510
Benzopinacol	a'	Hg	−0.58	X	413
	Azo, Hydrazo, and Related Compounds				
Azobenzene	A	Pt	1.33	Z	820
Hydrazobenzene	A	Pt	0.18, 1.35^a	Z	820
	A^c	Pt	0.05	Z	820
4,4’-Dichloroazobenzene	A	Pt	1.44	Z	820
4,4’-Dichlorohydrazobenzene	A	Pt	0.26, 1.44^a	Z	820
	A^c	Pt	0.16	Z	820
4,4’-Dimethoxyazobenzene	A	Pt	0.98	Z	820
	A^c	Pt	0.98, 1.25^a	Z	820
2,2’,4,4’-Tetrachloroazobenzene	A	Pt	1.59	Z	820
sym-Hexachloroazobenzene	A	Pt	1.63	Z	820
9-Hydrazoacridine	$A^{b'}$	Pt	−0.350	Y	92
Isonicotinic hydrazide	*z*	Hg	−0.28	X	508
1-Isonicotinoyl-2-phenylhydrazine	*z*	Hg	−0.24	X	508
Diphenylpicrylhydrazyl	A	Pt	0.70	X	737
Hydrazine	a'	Hg	−0.548	c'	450
Monomethylhydrazine	a'	Hg	−0.634	c'	450
n-Propylhydrazine	a'	Hg	−0.689	c'	450
n-Hexylhydrazine	a'	Hg	−0.791	c'	450
1,1-Dimethylhydrazine	a'	Hg	−0.694	c'	450
1,2-Dimethylhydrazine	a'	Hg	−0.698	c'	450
1,2-Diisobutylhydrazine	a'	Hg	−0.757	c'	450
Phenylhydrazine	a'	Hg	−0.752	c'	450
 R is S, Se, –CH=CH, NCH_3, studied at pH 10 in aqueous media at Pt					364
	Sulfur Compounds				
n-Propyl mercaptan	A	Pt	1.14	Z	503
Dimethyl disulfide	A	Pt	0.91, 1.59^a	Z	503
Thioglycolic acid	*j*	Hg	−0.30	X	483
Cysteine	*o*	Hg	−0.05	X	444
	t	Pt	Near 0.6	X	444
Mercaptobenzothiazole	*e*	Hg	−0.23	X	688
	Aldehydes and Ketones				
Anisaldehyde	A	Pt	1.63	Z	510
4-Methyl-2,6-heptanedione	A	Pt	1.28	Y	71
4-Methyl-3,5-heptadien-2-one	A	Pt	0.64	Y	71
1,5-Diphenyl-1,5-pentanedione	A	Pt	2.10	Y	71
1,3,5-Triphenyl-1,5-pentanedione	A	Pt	1.80	Y	71

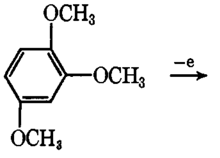
TABLE I (*Continued*)

Compound	Solvent system		$E^1/_2$	Ref electrode	Ref
	Other Functions				
Uric acid	*j*	Graphite	0.33 $E_{p/2}$	X	743
Parabanic acid	*j*	Graphite	−0.84	X	743
Tetra-*n*-propylammonium acetate	A	Pt	1.6	X	308

[a] Second oxidation wave. [b] Third oxidation wave. [c] Pyridine added. [d] DMF, perchlorate electrolyte. [e] Aqueous solution, pH 7. [f] Reference, Ag|AgCl. [g] 1.00 *M* aqueous H_2SO_4. [h] 49 compounds studied in CH_3CN. [i] All studied in aqueous solution [j] Aqueous buffered solution, pH 5.6. [k] 0.14 *M* aqueous LiCl. [l] $CH_3CN–H_2O$, $(CH_3)_4NOH$. [m] CH_2Cl_2, $(n\text{-}C_4H_9)_4NClO_4$. [n] Reference, nhe. [o] Aqueous solution, pH 1.0. [p] 1 *N* H_2SO_4. [q] 9 *N* H_2SO_4. [r] 0.1 *N* H_2SO_4. [s] Reference, normal calomel electrode. [t] Aqueous solution, pH 2. [u] Aqueous solution, pH 10. [v] Reference, Hg|Hg^{2+} (0.01 *M*). [w] Aqueous solution, pH 4.8. [x] Glycol dimethyl ether, $(n\text{-}C_4H_9)_4NClO_4$. [y] Reference, Ag|$Ag^+$ (0.001 *M*). [z] Aqueous solution, pH 13. [a'] 0.1 *N* aqueous NaOH. [b'] Diphenylguanidine added. [c'] Reference, saturated Hg_2SO_4. [d'] 60 compounds studied at pH 11 (aqueous) at Pt. [e] 19 compounds studied in neutral and acidic aqueous solution at Pt. [f'] Aqueous solution, pH 3.6. [g'] Aqueous solution, pH 9.2. [h'] 1 *N* aqueous NaOH.

Equation 1 is analogous to that proposed for the reaction of hydroquinone dimethyl ether in basic methanolic solution. Here the anodically generated species is trapped as the stable benzoquinone diketal (section III.A.2).

Dimerization of aromatics appears to be a general reaction of aromatic hydrocarbons, not only in aqueous media but in a variety of other solvents. An excellent yield of 2,4,5,2′,4′,5′-hexamethoxybiphenyl (3) is obtained by oxidation of 1,2,4-trimethoxybenzene (1) in aqueous acid solution at a PbO_2 anode (188). The reaction could occur by a number of pathways including dimerization of the anodically generated cation radical 2 or reaction of a cation radical or a dication with a neutral molecule of 1,2,4-trimethoxybenzene (Eq 2 and 3a, b, c, respectively).



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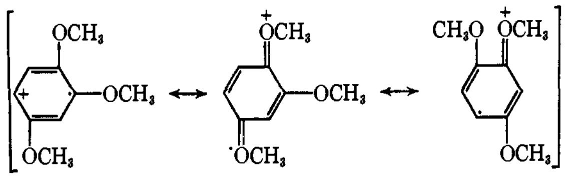
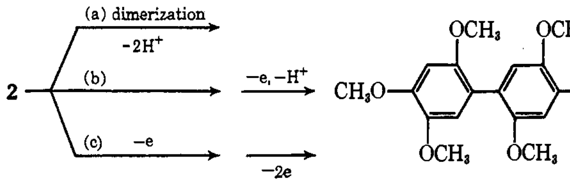


(Eq 2)

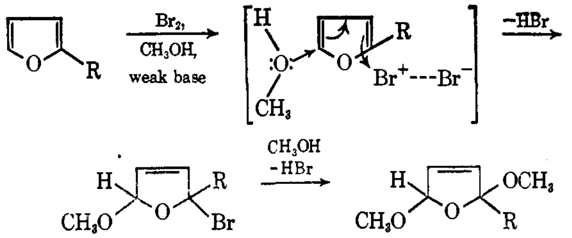
2



3 (Eq 3)

2. *Alkoxylation*

The electrooxidation of unsaturated organic compounds (of suitably low discharge potential) in alcoholic media leads to products such as ethers and acetals resulting from addition or substitution by alkoxy (R–O) groups. The Clauson-Kaas alkoxylation of substituted furans is the most thoroughly studied reaction of this kind. This area has been particularly successful as a novel and practical route to 2,5-dimethoxy-2,5-dihydrofurans (4), which are valuable precursors to a variety of compounds, including pyridines, pyridazines, pyrroles, and benzenoid compounds (109, 178). The reaction was conceived as a logical alternative to the chemical method of preparation of **4** in which furans are treated with methanolic bromine solution (113, 178, 393, 536). A likely route for the chemical reaction is depicted by Eq 4. Several disadvantages are inherent in the chemical method. These include the use of large quantities of bromine and the resultant contamination of the product with halogen-containing impurities which eventually cause decomposition of the acid-sensitive acetals. Moreover, the chemical method affords very poor yields of product from negatively substituted furans.



(Eq 4)

4

On the other hand, the anodic oxidation of furans in alcoholic solution containing NH_4Br as the electrolyte provides cleaner products of generally higher stability and yield. Bromide ion, both from the electrolyte and the hydrogen bromide evolved in the process, is oxidized to bromine and recycled in the methoxylation reaction. The electrolysis is carried out at approximately constant cell voltage (the current falls as the reaction proceeds). In spite of the uncontrolled potential conditions, the yields and current efficiencies are generally excellent. Under the above conditions there is no marked difference in yields on varying the anode material, suggesting that the electrochemical process involves solely discharge of halide ion (442).

A second reaction route appears to be operative since other nonhalide electrolytes provide the same products

TABLE II

OXIDATION OF AROMATIC COMPOUNDS IN AQUEOUS MEDIA[a]

Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
Benzene (H_2O, H_2SO_4 or $HClO_4$, various "oxygen" carriers)	Pt, PbO_2, C	Benzoquinone (81.5), phenol, catechol, maleic acid CO_2, CO, HCO_2H	261, 310, 360, 370, 382, 793, 837, 862
Toluene (H_2O, H_2SO_4 or HNO_3, various "oxygen carriers")	Pt, PbO_2	Benzaldehyde (20), *o*-cresol, *p*-cresol, 2-methylhydroquinone, 2-methylbenzoquinone, *p*-methylcatechol, benzoquinone	148, 261, 267 402, 472, 517, 554, 809
Ethylbenzene (H_2O, acetone, H_2SO_4)	Pt, PbO_2	Methylphenylcarbinol (4), acetophenone, benzaldehyde (6), *p*-hydroxyethylbenzene, benzoquinone, 2,2'-dihydroxy-5,5'-diethylbiphenyl	473–475, 606
Isopropylbenzene (H_2O, H_2SO_4)	Pt	2-Phenylpropionaldehyde, benzaldehyde	473–475
o-Xylene (H_2O, acetone, H_2SO_4)	Pt, PbO_2	*o*-Methylbenzaldehyde (24–35), *o*-toluic acid (9), 3,4-dimethylphenol (2), di-*o*-xylene (39), 3,4-dimethyl-4-hydroxy-2,5-cyclohexadienone, 2-methylbenzoquinone (9), 2,6-dimethylhydroquinone, 2,6-dimethylbenzoquinone	240, 474, 475
m-Xylene (H_2O, acetone, H_2SO_4)	Pt, PbO_2	*m*-Methylbenzaldehyde, *m*-toluic acid, isophthalic acid, 2,4-dimethylphenol, 2-methylbenzoquinone, 2,4-dimethyl-4-hydroxy-2,5-cyclohexadienone, 2,5-dimethylhydroquinone, 2,5-dimethylbenzoquinone, 2,2'-dihydroxy-3,5,3',5'-tetramethylbiphenyl	232, 472, 475
p-Xylene (H_2O, acetone, H_2SO_4)	Pt, PbO_2	*p*-Methylbenzaldehyde, *p*-toluic acid, terephthalaldehydic acid, terephthalic acid, *p*-carboxybenzalacetone, 2,5-dimethylphenol, 2,5-dimethylbenzoquinone, 4,4'-dihydroxy-2,5,2',5'-tetramethylbiphenyl, 2,5-dimethylhydroquinone	219, 239, 261, 475, 712
Mesitylene (H_2O, acetone, H_2SO_4)	Pt, PbO_2	3,5-Dimethylbenzaldehyde (10–15), 3,5-dimethylbenzoic acid, 2,4,6-trimethylphenol, 2,6-dimethylbenzoquinone, 2-hydroxy-3,5-dimethylbenzoic acid, HOAc, HCO_2H, CO_2, 5-methylisophthalic acid	234a, 472
1,2,4-Trimethylbenzene (H_2O, H_2SO_4)	Pt, PbO_2	2,4-Dimethylbenzaldehyde, 2,4-dimethylbenzoic acid, 3,4-dimethylbenzaldehyde, 3,4-dimethylbenzoic acid, 2-methylterephthalic acid, 2,4-dimethylphenol, 2-methylbenzoquinone, CO_2	244a, 472
1-Methyl-4-isopropylbenzene (H_2O, acetone, H_2SO_4)	Pt, PbO_2	*p*-Isopropylbenzyl alcohol, *p*-isopropylbenzaldehyde (7.8), *p*-isopropylbenzoic acid, *p*-propenylbenzoic acid, *p*-acetylbenzoic acid (12.3), terephthalic acid (11.8), 2-methyl-5-isopropylphenol	233, 474
Anisole (H_2O, H_2SO_4)	PbO_2	Benzoquinone (71.6), CH_3OH	215
Phenyl isoamyl ether (H_2O, H_2SO_4)	PbO_2	Benzoquinone (45), isovaleric acid, CO_2	215
Methyl *o*-cresol ether (H_2O, H_2SO_4)	PbO_2	2-Methylhydroquinone (20), 3,3'-dimethyl-4-hydroxy-4'-methoxybiphenyl, CH_3OH	242
Methyl *m*-cresol ether (H_2O, H_2SO_4)	PbO_2	2-Methylhydroquinone (30), 2,2'-dimethyl-4-hydroxy-4'-methoxybiphenyl (19), CH_3OH	242
Methyl *p*-cresol ether (H_2O, H_2SO_4)	Pt, PbO_2	Anisaldehyde (35), anisic acid (8), 2,2'-dimethoxy-5,5'-dimethylbiphenyl (21), 2-hydroxy-2'-methoxy-5,5'-dimethylbiphenyl, CH_3OH	242
Veratrole (H_2O, H_2SO_4)	PbO_2	3,4,3',4'-Tetramethoxybiphenyl, 4-hydroxy-3,3',4'-trimethoxybiphenyl, succinic acid	215
Hydroquinone dimethyl ether (H_2O, H_2SO_4)	PbO_2	Benzoquinone (48.6)	215
1,2,3-Trimethoxybenzene (H_2O, acetone, H_2SO_4)	PbO_2	2,6-Dimethoxybenzoquinone (30–36)	188
1,2,4-Trimethoxybenzene (H_2O, acetone, H_2SO_4, Na_2SO_4)	PbO_2	2,4,5,2',4',5'-Hexamethoxybiphenyl (85)	188
Nitrobenzene (H_2O, H_2SO_4)	PbO_2	Maleic acid	261
o-Nitrotoluene (HOAc, H_2SO_4)	Pt	*o*-Nitrobenzyl alcohol (17.9)	209, 633
m-Nitrotoluene (HOAc, H_2SO_4)	Pt	*m*-Nitrobenzaldehyde (18.1), *m*-nitrobenzoic acid	209, 633
p-Nitrotoluene (HOAc, H_2SO_4)	PbO_2	*p*-Nitrobenzyl alcohol (40), *p*-nitrobenzaldehyde, *p*-nitrobenzoic acid	157, 171, 209, 463
2,4-Dinitrotoluene (H_2O, H_2SO_4, CrO_3)	Pt, PbO_2	2,4-Dinitrobenzoic acid (74)	79, 685
2,4,6-Trinitrotoluene (H_2O, H_2SO_4)	Pt, PbO_2	2,4,6-Trinitrobenzoic acid (25)	686
Benzyl cyanide (H_2O, H_2SO_4)	PbO_2	Benzaldehyde (1.1), benzoic acid (24), NH_3 (18)	219
Benzonitrile (H_2O, H_2SO_4)	PbO_2	1,2,4-Trihydroxybenzene, 2,5-dihydroxybenzonitrile	219
o-Methylbenzonitrile (H_2O, H_2SO_4)	PbO_2	*o*-Cyanobenzoic acid (6.2)	219
m-Methylbenzonitrile (H_2O, acetone, H_2SO_4)	PbO_2	*m*-Cyanobenzoic acid (28)	219
p-Methylbenzonitrile (H_2O, acetone, H_2SO_4)	PbO_2	*p*-Cyanobenzoic acid (37), terephthalic acid (7.5)	219
2,4-Dimethylbenzonitrile (H_2O, H_2SO_4)	PbO_2	3-Methyl-4-cyanobenzoic acid (12)	245
Indan (*t*-BuOH, H_2O, NaOH, R_4NOH[b])	Pt	Indan (35), indanone (5), α-hydroxyindan (3), α-*t*-butoxyindan (8)	395
Tetralin (*t*-BuOH, H_2O, NaOH, R_4NOH[b])	Pt	Tetralin (42), α-tetralone (21), α-hydroxytetralin (9), α-*t*-butoxytetralin (9)	395

TABLE II (*Continued*)

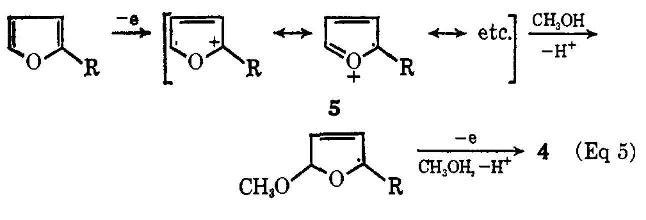
Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
6-Methoxytetralin (*t*-BuOH, H_2O, NaOH, R_4NOH^b)	Pt	6-Methoxytetralin (25), 6-methoxy-α-tetralone (40), 6-methoxy-α-hydroxytetralin (4)	395
p-Propylanisole (*t*-BuOH, H_2O, NaOH, R_4NOH^b)	Pt	*p*-Methoxypropiophenone (13)	395
Naphthalene (H_2O), H_2SO_4)	Pt, PbO_2	α-Naphthol, 1,4-naphthaquinone (30), phthalic acid	198, 603a, 834
α-Methylnaphthalene (H_2O, acetone, H_2SO_4)	PbO_2	1,1′-Dimethyl-4,4′-binaphthyl (10.5)	221
Anthracene (H_2O, H_2SO_4)	Pt, PbO_2	9,10-Anthraquinone (90)	198, 285, 437, 477, 655, 713, 779
Anthraquinone (concd H_2SO_4)	Pt	Alizarin + quinizarin (90), purpurin, alizarin–cyanin	656
Phenanthrene (H_2O, H_2SO_4, $Ce(SO_4)_2$)	PbO_2	Phenanthraquinone, α,α′-diphenyldicarboxylic acid, benzoic acid	198

[a] ArX where X is H, alkyl, alkoxyl, nitro, or cyano. [b] Cyclohexyltrimethylammonium hydroxide.

although often in poorer yield (441, 442). The anode material is important with these electrolytes, especially in basic media. At a Pt anode the yields of **4** (R = H) from furan with various electrolytes are in the order $NH_4Br \gg BF_3 > H_2SO_4 > NaNO_3, NH_4NO_3, NaO_2CH$ (117). With negatively substituted furans, NH_4Br or KOH gives little or no product, and H_2SO_4 must be used (110). Clearly a mechanism similar to Eq 1 does not apply with these electrolytes.

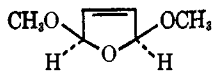
Suggestions have been made recently that the reaction scheme may involve discharge of CH_3OH to methoxy radicals which undergo 1,4 addition to the furan ring (25, 442). Indeed, it is conceivable that in basic solution methoxide ion may be discharged in this manner. However, scant evidence exists to substantiate methoxy radical involvement in the reaction. Little is known concerning the nature of such electrochemically generated species (26, 422, 485, 631, 690). In acid solution CH_3OH undergoes electrooxidation by initial homolytic cleavage of a C–H bond rather than the O–H bond in agreement with chemical studies and bond dissociation energies (α-C–H bond, 90 kcal/mole; O–H bond, 108 kcal/mole) (421).

A mechanism involving the reaction of cation radical **5** with solvent, followed by reoxidation and solvolysis to the final product **4**, appears justifiable (Eq 5) (628). Thus the successful methoxylation of negatively substituted furans may require H_2SO_4 as electrolyte to extend the useful anodic limit of the solvent to the point at which the furan may be discharged. (In acidic media, CH_3OH is discharged about 0.5 V more anodic than in basic solution.) It is significant that a wide range of substituents (ethers, acetals, alcohols, acetates, esters, amides, and ketones) are stable under these conditions, since generation of methoxy radicals would be expected to yield products derived from such side reactions as hydrogen abstraction and dimerization (325).



In a number of cases the *cis* and *trans* isomers which may exist have been isolated in pure form. A small excess of *cis* isomer **6** over *trans* isomer **7** is found in the electrolysis of furan. On the other hand, the furandiol **8** reportedly provides only the *trans*-intramolecular alkoxylation product **9** (642).

Thiophene also undergoes alkoxylation, affording 2,5-dimethoxy-2,5-dihydrothiophene (**10**) and malealdehyde tetramethyl acetal (441).



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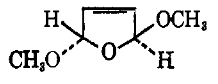

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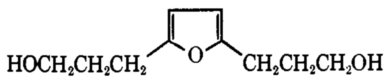

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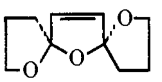

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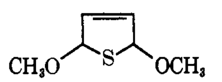

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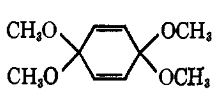
Attempted electrolysis of benzene and methyl benzoate in acidic or basic methanolic solutions gave no alkoxylation products (827), but aromatic ethers are readily oxidized to provide substitution and nonaromatic products (41). Using KOH as the electrolyte hydroquinone dimethyl ether provides an excellent yield of 3,3,6,6-tetramethoxy-1,4-cyclohexadiene (**11**).



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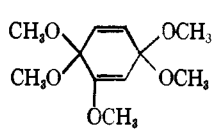

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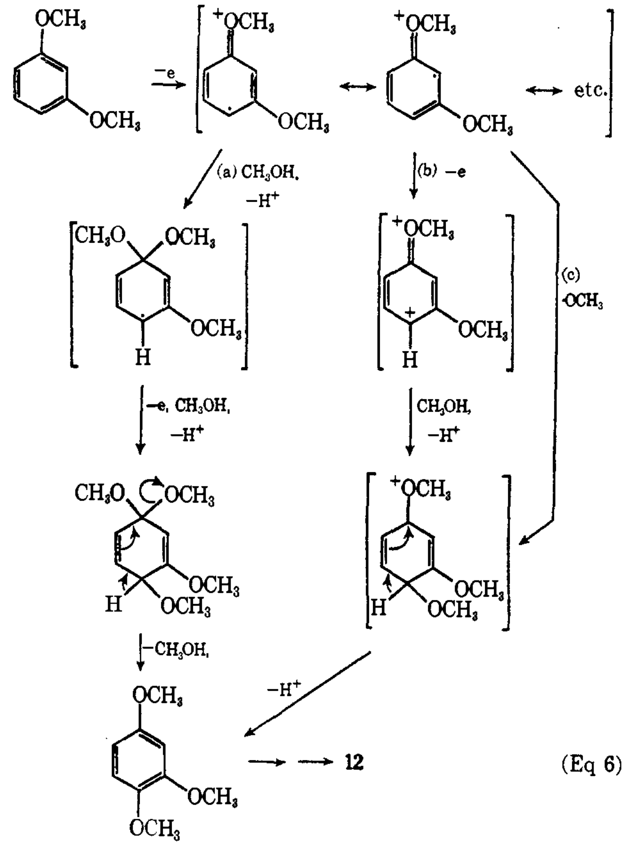
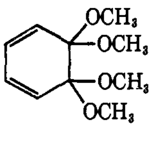
Resorcinol dimethyl ether is oxidized to 2,3,3,6,6-pentamethoxy-1,4-cyclohexadiene (**12**), an unidentified polymethoxylated compound, and a small amount of 1,2,4-trimethoxybenzene. The latter was identified as an intermediate in the reaction and was readily converted



(Eq 6)

to 12 under the same conditions. An experiment using resorcinol dimethyl ether labeled with $OC^{14}H^3$ established that there was no decrease in the specific radioactivity on formation of **12**. This result would exclude a mechanism such as 6a and favor either pathway 6b or 6c.

By far the most interesting products were provided by the methoxylation of veratrol. Here, in addition to the products of oxidation of resorcinol dimethyl ether, 5,5,6,6-tetramethoxy-1,3-cyclohexadiene (**13**), and hexamethyl *cis,cis*-orthomuconate (**14**) were ob-



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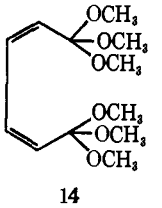
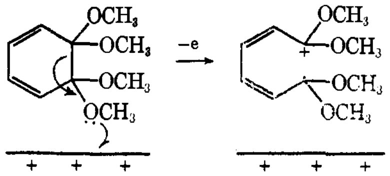


14

tained. That **13** is a precursor of **14** was confirmed by electrolysis of the *o*-quinone diketal **13** to the diortho ester **14** in 77% yield. It is conceivable that this ring-opening reaction, aided by the large steric and dipole interaction existing among four ether groups, may occur *via* electron transfer through an ether oxygen (Eq 7) followed by reaction with solvent, reoxidation, and solvolysis to **14**. Significantly, only the least stable *cis,cis* isomer of the three possible diortho esters is formed, suggesting that the intermediate species are



(Eq 7)

not long-lived and that an adsorption process may be involved in maintaining the *cis,cis* configuration.

Anodic methoxylation and acetoxylation (section III.A.3) of anisole appear to be similar reactions. Table III compares the results of these reactions for the *ortho*, *meta*, and *para* product distribution under conditions of low conversion (less than 5% of reaction allowed to proceed). A concerted mechanism involving a two-electron transfer from anisole with formation of a C–O bond has been suggested for acetoxylation and may be applicable to alkoxylation (164). This scheme is similar to that proposed for electrophilic aromatic substitution in homogeneous solution (323).

TABLE III

ISOMER DISTRIBUTION IN METHOXYLATION AND ACETOXYLATION OF ANISOLE

	o	m	p
Methoxylation	39	3	58
Acetoxylation	67.4	3.5	29.1

Electrolysis of hydroquinone dimethyl ether in basic methanolic solution under controlled-potential conditions results in a decrease in the yield of product **11** as the potential is lowered (Table IV). These results imply that alkoxylation of aromatics must involve a cation radical or dication species. Since the data were obtained above the discharge potential of the solvent (cooxidation of solvent occurs), a decision between mechanisms such as pathway 6b or 6c is not possible. The increased oxidation of hydroquinone dimethyl ether relative to solvent at higher potentials is remarkable and may suggest that the aromatic is preferentially adsorbed before charge transfer occurs.

TABLE IV

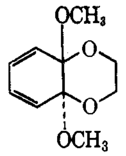
METHOXYLATION OF HYDROQUINONE DIMETHYL ETHER (827)

	Products, mole %[b]	
cpe *vs.* sce,[a] V	Starting material	Quinone diketal **11**
1.45	34.9	65.1
1.10	49.2	50.8
1.00	81.3	18.7

[a] The three runs were carried out under identical conditions allowing the passage of 2 faradays/mole. [b] Calculated from nmr spectrum of crude product.

Intramolecular alkoxylation of hydroquinone bis(β-hydroxyethyl) ether occurs in methanolic solution to provide a good yield of the ketal **15**. The methoxylation of benzodioxane affords the *trans*-*o*-quinone diketal **16** in 31% yield (287, 826).

15



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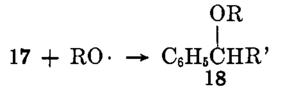
A number of alkyl-substituted aromatics are electrochemically alkoxylated at the α position. In view of their relatively high oxidation potentials (section II.-A.2), discharge of the aromatic ring appears unlikely compared to oxidation of electrolyte or solvent. This would imply a radical abstraction mechanism (Eq 8–13), whereby an α-alkyl radical **17** results. The latter could react with an alkoxy radical or undergo further

$$ROH + OH^- \rightarrow RO^- + H_2O \qquad \text{(Eq 8)}$$

$$RO^- \rightarrow RO\cdot + e \qquad \text{(Eq 9)}$$

$$RO\cdot + C_6H_5CH_2R' \rightarrow ROH + \underset{17}{C_6H_5\dot{C}HR'} \qquad \text{(Eq 10)}$$

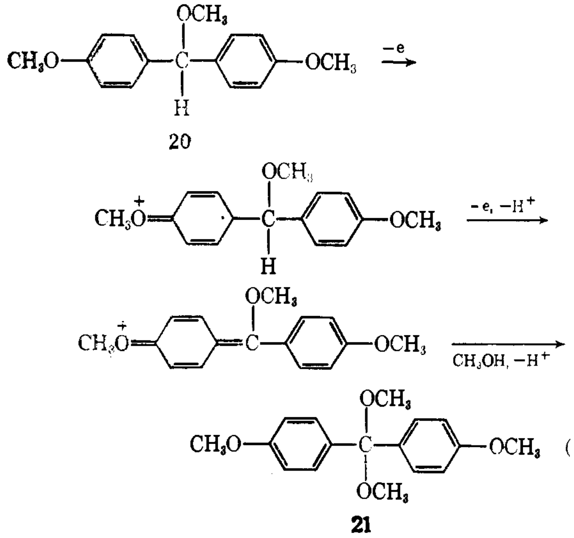


$$17 + RO\cdot \rightarrow \underset{18}{C_6H_5\overset{OR}{C}HR'} \qquad \text{(Eq 11)}$$

$$17 \rightarrow \underset{19}{C_6H_5\overset{+}{C}HR'} + e \qquad \text{(Eq 12)}$$

$$19 + ROH \rightarrow 18 + H^+ \qquad \text{(Eq 13)}$$

oxidation to the benzylic cation **19**, ultimately providing the product **18**. A similar scheme has been postulated (369) on the basis of a number of arguments including the position of substitution and the relative reactivity of hydrocarbons (tetralin > indan > diphenylmethane)—results that parallel free-radical reactions with peroxy, *t*-butoxy, and methyl radicals (549, 683, 838). Chemically generated methoxy radicals, however, react with aromatic hydrocarbons to provide high yields of CH_3OH and benzylic dimers and no methoxylated product (325, 525). Anodically adsorbed radicals may be considerably different in their reaction characteristics from those formed in homogeneous solution. Some experimental evidence has recently appeared which supports the role of electrolyte radicals in these reactions (691).



20

(Eq 14)

21

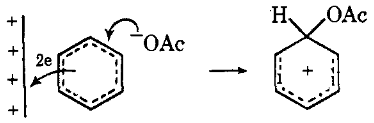
In contrast, the methoxylation of *p,p'*-dimethoxydiphenylmethyl methyl ether (**20**) to *p,p'*-dimethoxybenzophenone dimethyl acetal (**21**) could proceed by direct charge transfer of the aromatic hydrocarbon (Eq 14) since **20** should have a relatively low discharge potential (846).

A summary of electrochemical alkoxylations of aromatics is given in Table V.

3. Acyloxylation

Acetoxylation of aromatic substrates has often been cited as evidence for the existence of acetoxy radicals in the Kolbe reaction (338, 493, 841). Recent studies have demonstrated that acetoxy radicals are intermediates in the Kolbe synthesis, but not in the formation of ring-substituted aromatic acetates (161). Aromatic compounds are generally discharged below the critical potential for oxidation of acetate ion (1.9–2.1 V *vs.* sce) and undergo what appears to be an electrophilic substitution reaction. In homogeneous solution the lifetime of the acetoxy radical (10^{-9}–10^{-10} sec) is estimated to be too short for reaction outside of the solvent cage in which it is formed (350). Indeed there is presently no evidence of homogeneous acetoxylation of aromatics by acetoxy radicals (produced in thermal decomposition of diacetyl peroxide) (839).

These results suggest that the substrate undergoes electron transfer to form a cationic species which reacts with acetate ion. Both cation radical and dication mechanisms in addition to a concerted two-electron transfer to the anode followed by C–O bond formation have been proposed (161, 627). The latter mechanism (Eq 15) is comparable to electrophilic substitution and is supported by isotope effect determinations and studies of isomer distributions for a number of anodic acetoxylation reactions. In addition to the isomer distributions shown in Table VI, Eberson (164) has tabulated the results for acetoxylation of isopropylbenzene, diphenylmethane, fluoro-, chloro-, bromo-, and iodobenzenes, biphenyl, and naphthalene. Significantly anodic acetoxylation does not occur with negatively substituted aromatics whose half-wave potentials are more anodic in value than the discharge of acetate.



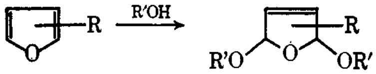
(Eq 15)

By carrying out the electrolysis of anisole under cpe conditions (1.50 V *vs.* sce) but with only 50% of the theoretically calculated current, the yield of products (*o*- and *p*-acetoxyanisoles) could be raised from 27 to

TABLE V

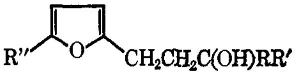
ELECTROCHEMICAL ALKOXYLATION OF AROMATICS

Oxidation of Furans:



R (solvent, electrolyte)	Anode	% yield of 2,5-dialkoxy-2,5-dihydrofuran	Ref
2-Substituted furans			
H (CH_3OH, NH_4Br)	Pt, C	78[a,g]	109, 111, 117, 139, 441, 639, 640, 814
(C_2H_5OH, NH_4Br)	Pt	63[b]	105, 441
(i-C_3H_7OH, NH_4Br)	Pt	23	111
(n-C_3H_7OH, diethanolamine hydrobromide)	Pt	31	111
CH_3 (CH_3OH, NH_4Br)	Pt, C	85	111, 112, 139, 639, 640
CH_2OH (CH_3OH, NH_4Br)	Pt	66	112, 115
CH_2OCH_3 (CH_3OH, NH_4Br)	Pt	83	104, 111, 139
CH_2OAc (CH_3OH, NH_4Br)	Pt, C	87	112, 639, 640, 736
$CH(OCH_3)_2$ (CH_3OH, NH_4Br)	Pt	82	112
$C(OCH_3)_2CH_3$ (CH_3OH, NH_4Br)	Pt	64	106, 115
CO_2CH_3 (CH_3OH, KOH)	Pt	0[c]	827
(CH_3OH, H_2SO_4)	Pt	68[d]	110
$CO_2C_2H_5$ (C_2H_5OH, H_2SO_4)	Pt	61.5	577
$CH(OH)CH_3$ (CH_3OH, NH_4Br)	Pt	73	114
$COCH_3$ (CH_3OH, H_2SO_4)	Pt	29	828
$CH(OAc)CH_2NHAc$ (CH_3OH, NH_4Br)	Pt	>38[e]	114
$CH(NHAc)CH_3$ (CH_3OH, NH_4Br)	Pt	88	107, 108
$CH(NHCO_2CH_3)CH_3$ (CH_3OH, NH_4Br)	Pt	88	107, 108
$CH_2NH(CO_2CH_3)$ (CH_3OH, NH_4Br)	Pt	89	107, 108
$CH_2NH(CO_2CH_3)$ (CH_3OH, NH_4Br)	Pt	89	107
$CH(NHCONH_2)CH_3$ (CH_3OH, NH_4Br)	Pt	>62[f]	107
$CH_2CH(CO_2CH_3)_2$ (CH_3OH, NH_4Br)	Pt	74	177
CH_2NHAc (CH_3OH, NH_4Br)	Pt	96[g]	116
$CH_2NHCOC_6H_5$ (CH_3OH, NH_4Br)	Pt	27 + 47[g]	520
$CH_2CH_2CH(OAc)CH_3$ (CH_3OH, NH_4Br)	C	67	639, 640
$CH_2CH_2COCH_3$ (CH_3OH, NH_4Br)	C	52	639, 640
$CH_2N(Ac)CH_2CH_2OAc$ (CH_3OH, NH_4Br)	C	55[e]	639, 640
$CH_2CH_2CH(CH_3)C_2H_5$ (CH_3OH, NH_4Br)	C	51	639, 640
$CH_2CH_2CH_2OAc$ (CH_3OH, NH_4Br)	C	47	639, 640
$CH{=}CHCO_2C_2H_5$ (CH_3OH, H_2SO_4)	Pt	51	578
2,5-Disubstituted Furans			
2 — 5			
CO_2CH_3 — i-C_3H_7 (CH_3OH, H_2SO_4)	Pt	87	107, 114
CO_2CH_3 — t-Butyl (CH_3OH, H_2SO_4)	Pt	97	114
CH_2OAc — CH_2NHAc (CH_3OH, NH_4Br)	Pt	>74[h]	180
CH_3 — CH_3 (CH_3OH, $NaOCH_3$)	..	..	25
CO_2CH_3 — Br (CH_3OH, H_2SO_4)	Pt	38.5[i]	578
$CO_2C_2H_5$ — Br (CH_3OH, H_2SO_4)	Pt	57[j]	578
Substituted Furans			
3-Isopropylfuran (CH_3OH, NH_4Br)	Pt	72	176
2-Carbomethoxy-4-isopropylfuran (CH_3OH, H_2SO_4)	Pt	61	176
2-Dimethoxymethyl-3-isopropylfuran (CH_3OH, NH_4Br)	Pt	75	176
sym-Difurfurylurea (CH_3OH, NH_4Br)	Pt	>85[k]	108
2-(α-N-Acetamidoethyl)-3,4-bis(acetoxymethyl)furan (CH_3OH, NH_4Br)	Pt	>76[l]	179

Intramolecular Alkoxylation of Furans:



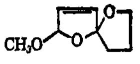
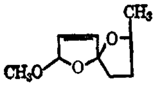
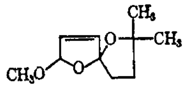
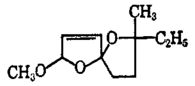
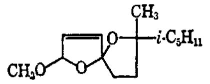
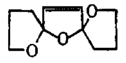
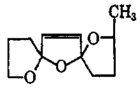
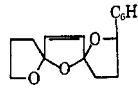
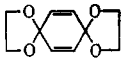
R	R'	R''	Solvent, electrolyte	Anode	Product (% yield)	Ref
H	H	H	CH_3OH, NH_4Br	C	 (53)	638, 641
H	CH_3	H	CH_3OH, NH_4Br	C	 (76)	638, 641
H	$CH_2CH(CH_3)_2$	H	CH_3OH, NH_4Br	C	 (75)	638, 641

TABLE V (*Continued*)

R	R′	R″	Solvent, electrolyte	Anode	Product (% yield)		Ref
CH_3	CH_3	H	CH_3OH, NH_4Br	C		(63)	638
CH_3	C_2H_5	H	CH_3OH, NH_4Br	C		(65)	638, 641
CH_3	i-C_5H_{11}	H	CH_3OH, NH_4Br	C		(35)	638
$CH_2CH_2CH_2OH$	H	H	CH_3OH, NH_4Br	C		(70)[m]	642, 643
$CH_2CH_2CH_2OH$	H	CH_3	CH_3OH, NH_4Br	C		(68)	642
$CH_2CH_2CH_2OH$	H	C_6H_5	CH_3OH, NH_4Br	C		(23)	642

Miscellaneous Alkoxylations

Aromatic (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
Methyl benzoate (CH_3OH, KOH or H_2SO_4)	Pt	No alkoxylation product	827
Benzene (CH_3OH, KOH)	Pt	No alkoxylation product	827
Anisole (CH_3OH, KOH)	Pt	*o*-, *m*-, *p*-Dimethoxybenzenes ($o:m:p$ = 39:3:58; mixture of quinone ketals)	827
Hydroquinone dimethyl ether (CH_3OH, KOH)	Pt	3,3,6,6-Tetramethoxy-1,4-cyclohexadiene (88)	41
Resorcinol dimethyl ether (CH_3OH, KOH)	Pt	1,2,4-Trimethoxybenzene (<5), 2,3,3,6,6-pentamethoxy-1,4-cyclohexadiene (61), unidentified product	41
Veratrole (CH_3OH, KOH)	Pt	1,2,4-Trimethoxybenzene (<5), 5,5,6,6-tetramethoxy-1,3-cyclohexadiene (15), 2,3,3,6,6-pentamethoxy-1,4-cyclohexadiene (15), hexamethyl *cis,cis*-orthomuconate (10)	41
1,2,4-Trimethoxybenzene (CH_3OH, KOH)	Pt	2,3,3,6,6-Pentamethoxy-1,4-cyclohexadiene (89)	41
9,10-Dimethoxyanthracene (CH_3OH, KOH)	Pt	9,9,10,10-Tetramethoxy-9,10-dihydroanthracene (32)	826
Benzodioxane (CH_3OH, KOH)	Pt	*trans*-4a,8a-Dimethoxy-4a,8a-dihydro-1,4-benzodioxan (31)	287, 826
Hydroquinone bis(β-hydroxyethyl) ether (CH_3OH, KOH)	Pt	 (60–70), higher molecular weight alcohols	829
Thiophene			
(a) (CH_3OH, NaBr)	C	2,5-Dimethoxy-2,5-dihydrothiophene (36)[n]	441
(b) (CH_3OH, H_2SO_4)	C	Malealdehyde tetramethyl acetal (26), methoxysuccindialdehyde tetramethyl acetal, β-formylpropionic acid,[n] SO_2	388
1-(3-Thienyl)ethanol acetate (CH_3OH, H_2SO_4)	C	3-Dimethoxymethyl-4-acetoxy-2-penten-1-al dimethyl acetal (46)	389
Methyl 3-(5-methyl-2-thienyl)propionate (CH_3OH, H_2SO_4)	C	Methyl 4,7-dioxo-5-octenoate dimethyl acetal (3.2 g/7.4 gsm),[n] SO_2	390

Alkoxylation of the Aromatic Side Chain

Aromatic (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
Toluene (CH_3OH, $NaOCH_3$)	Pt	Methyl benzyl ether (2), ring-substituted ethers (trace)	366, 691
Ethylbenzene (CH_3OH, $NaOCH_3$)	Pt	α-Methoxyethylbenzene (8.3), styrene	366, 691
Isopropylbenzene (CH_3OH, $NaOCH_3$)	Pt	α-Methoxyisopropylbenzene (11), α-methylstyrene	366, 691
Diphenylmethane (CH_3OH, $NaOCH_3$)	Pt	α-Methoxydiphenylmethane (3.4)	369
Tetralin[o]			
(a) (CH_3OH, $NaOCH_3$)	Pt	α-Methoxytetralin (22–29.1)	369
(b) (CH_3OH, HCN, NaCN)	Pt	α-Methoxytetralin (10 g/80 ml of sm), 6-cyanotetralin (1.3 g)	446
Indan[o] (CH_3OH, $NaOCH_3$)	Pt	α-Methoxyindan (15.1)	369
p-Methoxydiphenylmethyl methyl ether (CH_3OH, methyl hydrogen glutarate)	Pt	*p,p*′-Dimethoxybenzophenone dimethyl acetal (60)	846

[a] A small quantity of malealdehyde tetramethyl acetal is produced. [b] A small quantity of malealdehyde tetraethyl acetal is produced. [c] Starting material recovered. [d] *d*-Camphorsulfonic acid has been used successfully as the electrolyte with comparable yield (827). [e] Isolated as the amino alcohol. [f] Product isolated as 2-methyl-3-hydroxypyridine. [g] Mixture of *cis* and *trans* isomers separated. [h] Product isolated as 6-hydroxymethyl-3-pyridinol. [i] Product: 2,5,5-trimethoxy-2-carbomethoxy-2,5-dihydrofuran. [j] Product: 2,5,5-trimethoxy-2-carboethoxy-2,5-dihydrofuran. [k] Product not isolated but used directly in a subsequent synthesis. [l] Product isolated: pyridoxine. [m] Only *trans* isomer found. [n] Characterized as the 2,4-dinitrophenylhydrazone. [o] See section III.A.1 for reactions in aqueous *t*-butyl alcohol solution.

TABLE VI

ACYLOXYLATION OF AROMATIC COMPOUNDS

Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
Furan (HOAc, KOAc)	Pt[a]	2,5-Diacetoxy-2,5-dihydrofuran (45)	25, 441, 442
2,5-Dimethylfuran (HOAc, NaOAc)	...	2,5-Bis(acetoxymethyl)furan	25
Benzene (HOAc, KOAc)	Pt	Phenyl acetate,[b] catechol diacetate, hydroquinone diacetate	677a
Toluene			
(a) (HOAc, NaOAc), cpe 1.90 V *vs.* sce	Pt	Monoacetoxy toluenes, $o:m:p = 43.2:11.1:45.7$; benzylacetate	164, 338
(b) (HOAc, $(C_2H_5)_4NNO_3$)	Pt	Toluene (0.0231),[c] benzaldehyde (0.0070), benzyl acetate (0.0188), benzyl alcohol and benzyl nitrate (0.0096–0.0136), benzylidene diacetate (0.0007), bibenzyl (0.0011)	680
Ethylbenzene (HOAc, NaOAc), cpe 1.90 V *vs.* sce	Pt	α-,[b] *o*-, *m*-, *p*-Acetoxyethylbenzenes in distribution 0.48:0.28:0.07:0.24; cumene, 2-ethyltoluene, 3- and/or 4-ethyltoluene	164, 677a
t-Butylbenzene (HOAc, NaOAc), cpe 1.90 V *vs.* sce	Pt	*o*-, *m*-, *p*-*t*-Butylphenyl acetate in distribution 0.25:0.24:0.39; 4-*t*-butylcatechol diacetate	164, 677a
Mesitylene			
(a) (HOAc, KOAc)[e]	Pt	2,4,6-Trimethylphenyl acetate (29), 3,5-dimethylbenzyl acetate (11.5), 5-ethyl-*m*-xylene (7), isodurene (2)	167, 677a
(b) (HOAc, $(C_2H_5)_4NNO_3$)	Pt	Mesitylene (0.0425),[c] 3,5-dimethylbenzyl acetate (0.0130), 3,5-dimethylbenzyl nitrate (0.0132), 3,5-dimethylbenzaldehyde (0.0018), 2,4,6-trimethylphenyl acetate (0.0003), 3,3′,5,5′-tetramethylbibenzyl	680
Durene (HOAc, NaOAc), cpe 1.70 V *vs.* sce	Pt	2,4,5-Trimethylbenzyl acetate (46)	167
Hexamethylbenzene (HOAc, NaOAc), cpe 1.50 V *vs.* sce	Pt	Pentamethylbenzyl acetate (57)	167
Anisole			
(a) (HOAc, NaOAc),[f] cpe 1.5 V *vs.* sce	Pt	*o*- and *p*-Acetoxyanisole (40), $o:p = 6:1$	166, 167, 338, 342
(b) (Propionic acid)	Pt	Methoxyphenyl propionates (24)	342
(c) (Valeric acid)	Pt	Methoxyphenyl valerates (13)	342
(d) (CH_3CN, $(C_2H_5)_3N$, benzoic acid)	Pt	*o*- and *p*-Methoxyphenyl benzoate (60) $o:p = 2:1$, biphenyl, CO_2	447
(e) (CH_3CN, $(C_2H_5)_3N$, *p*-toluic acid)	Pt	*o*- and *p*-Methoxyphenyl *p*-toluate (52), $o:p = 3:2$	447
(f) (CH_3CN, $(C_2H_5)_3N$, *p*-anisic acid)	Pt	*o*- and *p*-Methoxyphenyl *p*-anisate (13.5), $o:p = 3:2$	447
Phenyl acetate (HOAc, NaOAc)[e]	Pt	1,2- and 1,4-Diacetoxybenzene (37), $o:p = 11:9$	167, 677a
1,4-Dimethoxybenzene (HOAc, KOAc)	Pt	2-Acetoxy-1,4-dimethoxybenzene (62)	826
p-Methoxytoluene (HOAc, Ac_2O, NaOAc)	Pt	*p*-Methoxybenzaldehyde, *p*-methoxybenzyl acetate,[b] 2-acetoxy-4-methylanisole, 3-acetoxy-4-methylanisole	164
Benzotrifluoride (HOAc, NaOAc), cpe 2.4 V *vs.* sce	Pt	No acetates formed	164
Methyl benzoate (HOAc, NaOAc), cpe 2.4 V *vs.* sce	Pt	No acetates formed	164
Biphenyl (HOAc, NaOAc), cpe 1.6 V *vs.* sce	Pt	2-Acetoxybiphenyl (15), 4-acetoxybiphenyl (22)	164, 167
Naphthalene			
(a) (HOAc, NaOAc), cpe 1.7 V *vs.* sce	Pt	1-Acetoxynaphthalene (16), 1- and 2-methylnaphthalenes (4)	166, 167, 338, 342, 482, 493, 677a
(b) (HOAc, NaOAc), cpe 1.50 V *vs.* sce	Pt	1-Acetoxynaphthalene (22), 1- and 2-methylnaphthalenes (1)	
(c) (HOAc, NaOAc), cpe 1.0 V *vs.* sce	Pt	1-Acetoxynaphthalene (24)	
(d) (HOAc, Ac_2O, NaOAc)	PbO_2	1- and 2-Acetoxynaphthalenes (29) 1:2 = 94.5:5.5, diacetoxynaphthalenes (8), higher acetates	435
(e) (CH_3CN, H_2O, NaOH, benzoic acid)	Pt	α-Naphthol (25),[d] 4-hydroxy-1,1'-binaphthyl (14)	840
1-Methylnaphthalene (HOAc, Ac_2O, NaOAc)	Pt	4-Methyl-1-naphthyl acetate (40)	434
2-Methylnaphthalene (HOAc, Ac_2O, NaOAc)	Pt	2-Methyl-1-naphthyl acetate + 2-methyl-4-naphthyl acetate (51), 2-methyl-1,4-diacetoxynaphthalene (9)	434
1-Naphthyl acetate (HOAc, Ac_2O, NaOAc)	PbO_2	Diacetoxynaphthalenes (22), 1,4,5,8-tetracetoxynaphthalene? (12), higher derivatives	435
Biphenyl-2-carboxylic acid (HOAc, NaOAc), cpe 1.75 V *vs.* sce	Pt	2'-Hydroxybiphenyl-2-carboxylic acid lactone (36)	167, 412
3'-Acetamidobiphenyl-2-carboxylic acid (H_2O, Na_2CO_3)	Pt	Recovered acid (16)	412
3'-Methoxybiphenyl-2-carboxylic acid (H_2O, Na_2CO_3)	Pt	5′-Methoxy-2′-hydroxybiphenyl-2-carboxylic acid lactone (21)	412
3'-Cyanobiphenyl-2-carboxylic acid (H_2O, Na_2CO_3)	Pt	5'-Cyano-2'-hydroxybiphenyl-2-carboxylic acid lactone (15)	412
3'-Nitrobiphenyl-2-carboxylic acid (H_2O, Na_2CO_3)	Pt	5'-Nitro-2′-hydroxybiphenyl-2-carboxylic acid lactone (2)	412
o-Benzoylbenzoic acid (CH_3OH, $NaOCH_3$)	Pt	3-Phenylphthalide, methyl phenyl phthalate (25)	84
o-(*p*-Chlorobenzoyl)benzoic acid (CH_3OH, $NaOCH_3$)	Pt	3-*p*-Chlorophenylphthalide, *p*-chlorophenyl methyl phthalate (25)	84
o-(*p*-Bromobenzoyl)benzoic acid (CH_3OH, $NaOCH_3$)	Pt	3-*p*-Bromophenylphthalide, *p*-bromophenyl methyl phthalate (25)	84

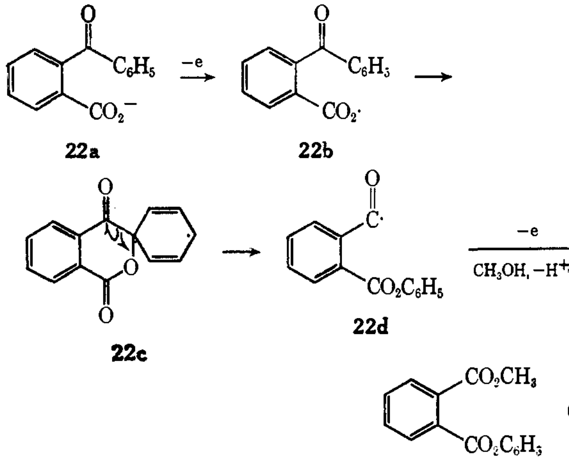
TABLE VI (*Continued*)

Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
3,3,3-Triphenylpropionic acid (CH_3OH, $NaOCH_3$)	Pt	Phenyl 3,3-diphenyl-3-methoxypropionate (16)	72
3,3,3-Tri-*p*-*t*-butylphenylpropionic acid (CH_3OH, $NaOCH_3$)	Pt	*p*-*t*-Butylphenyl 3,3-di-*p*-*t*-butylphenyl-3-methoxypropionate (23)	72
3,3-Diphenylpropionic acid			
(a) (HOAc, NaOAc, sodium salt of acid)	Pt	4-Phenyl-3,4-dihydrocoumarin^b (253 mg/5.37 gsm), 1,1-diphenylpropane, phenyl cinnamate, $C_6H_5CH(OAc)CH_2CO_2$-C_6H_5, $C_6H_5CH_2CH(C_6H_5)OAc$, $(C_6H_5)_2C(OH)CH_2OAc$	62
(b) (CH_3OH, $NaOCH_3$)	Pt	4-Phenyl-3,4-dihydrocoumarin, 1,1,4,4-tetraphenylbutane (13), $C_6H_5CH_2CH(C_6H_5)OCH_3$ (12.7), $C_6H_5CH(OCH_3)CH_2CO_2C_6H_5$	62
3,3-Diphenylacrylic acid			
(a) (HOAc, Ac_2O, KOAc)	C	4-Phenylcoumarin (35), 1,1-diphenylpropene (15), benzil (23), benzophenone (4), deoxybenzoin (5), 2,2-diphenylvinyl acetate (3), benzoin acetate (3)	436
(b) (CH_3OH, KOH)	C	4-Phenylcoumarin (58), benzil (4), benzophenone (4), methyl 3,3-diphenylacrylate (4)	436

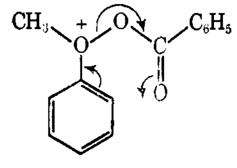
[a] The product could not be obtained with a graphite anode. [b] Major product. [c] Moles of product. [d] Products after saponification [e] Also carried out under cpe conditions. [f] Electrolyzed to 50% of theoretical current.

40%. Apparently, *p*-acetoxyanisole ($E_{1/2}$ = 1.12 V *vs.* sce) is oxidized destructively. In another case the methylation of naphthalene may be suppressed in favor of the acetoxylation process by operating at relatively low anode potentials. These examples further illustrate the importance of utilizing cpe (167).

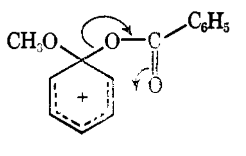
Intramolecular acyloxylations have been observed in a number of cases. An interesting example is the electrolysis of substituted benzoylbenzoic acid (**22a**). In methanolic $NaOCH_3$ a novel rearrangement occurs affording a mixture of 3-phenylphthalides and methyl phenyl phthalates (**22e**). The reaction is believed to proceed by intramolecular attack of the anodically generated benzoyloxy radical **22b** to form the radical **22c**, followed by rearrangement to the acyl radical **22d** (Eq 16). Further oxidation and solvolysis provide the phthalate **22e**. The formation of phenyl esters in the electrolysis of 3,3,3-triphenylpropionic acids has been postulated to involve an intermediate radical similar to **22c** (72). In contrast to acetoxylation, benzoyloxy radicals may be involved in the proposed scheme (Eq 16), and indeed in other anodic benzoyloxylation reactions, since homolytic benzoyloxylation has been reported in a number of nonelectrochemical examples (512). The benzoyloxy radical decarboxylates with an estimated rate constant of about 1 sec^{-1} (163). The high *ortho* to *para* ratio in these reactions has been attributed to formation of a complex such as **23**, derived from combination of the anisole cation radical and benzoyloxy radical (447, 512). The cation **23** may then undergo rearrangement to the *ortho* substitution product. However, formation of a σ complex **24** by combination of the same radical species, followed by rearrangement, could equally account for *ortho*-isomer preponderance.



(Eq 16)



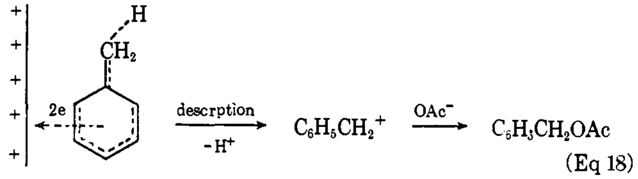
23



24

The side-chain anodic acetoxylation of aromatics has been described as proceeding *via* two consecutive electron transfers (Eq 17), or alternatively by a simultaneous two-electron transfer with cleavage of the α C–H bond to give benzyl cation (Eq 18) (164). The former route is similar to that ascribed to the oxidation of aromatic compounds by manganic acetate in HOAc (15, 16, 18). While nuclear acetoxylation requires the presence of acetate ion, side-chain acetoxylation can be achieved in acetic acid containing salts of other anions, such as perchlorate or tosylate. A primary deuterium

$$\begin{tikzcd}
C_6H_5CH_3 \arrow[r, "-e"] & {[C_6H_5CH_3]^{+\cdot}} \arrow[r, "-H^+"] & C_6H_5CH_2\cdot \arrow[d, "-e"] \\
& C_6H_5CH_2OAc & C_6H_5CH_2^+ \arrow[l, "OAc^-"']
\end{tikzcd} \qquad \text{(Eq 17)}$$



(Eq 18)

isotope effect $k_H:k_D$ of 2.6 ± 0.3 was observed for the side-chain anodic acetoxylation of ethylbenzene-α-d in HOAc containing NaOAc, implying C–H bond weakening in the transition state of the rate-determining step. An isotope effect has also been demonstrated for the manganic acetate oxidation of the methyl group of *p*-methoxytoluene (16). These results support the view that benzyl cations are intermediates in side-chain acetoxylations with acetate electrolyte, although the data do not permit distinction between routes 17 and 18.

In contrast, the oxidation of mesitylene and toluene in HOAc containing $(C_2H_5)_4NNO_3$ results almost exclusively in substitution of the side chain rather than the ring. Moreover, the products which include benzyl nitrates, benzyl acetates, and especially bibenzyls suggest a mechanism involving hydrogen abstraction by nitrate radical formed in the discharge of nitrate ion (Eq 19–23) (680). The anodic methoxylation of the side chain of alkyl-substituted aromatics has been described in a similar manner (section III.A.2) (691).

$$NO_3^- \rightarrow NO_3\cdot + e \qquad \text{(Eq 19)}$$

$$NO_3\cdot + RCH_3 \rightarrow HNO_3 + RCH_2\cdot \qquad \text{(Eq 20)}$$

$$2RCH_2\cdot \rightarrow RCH_2CH_2R \qquad \text{(Eq 21)}$$

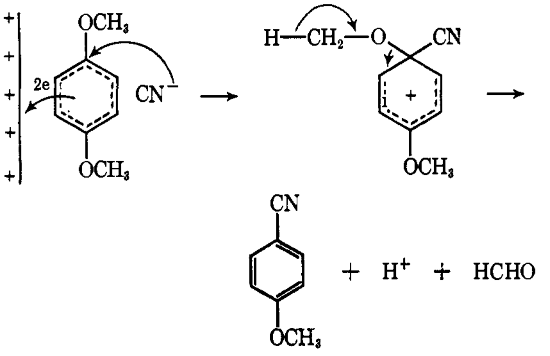
$$RCH_2\cdot \rightarrow RCH_2^+ + e \qquad \text{(Eq 22)}$$

$$RCH_2^+ + X^- \rightarrow RCH_2X\ (X, NO_3^-, OAc^-, OH^-) \qquad \text{(Eq 23)}$$

4. Cyanation

A study of the anodic discharge of cyanide ion has established that the reaction constitutes a one-electron oxidation with $E_{1/2}$ about 0.6 V *vs.* sce in aqueous solution (at Pt; pH 8–11) (692). Cyanation of anisole in methanolic solution occurs only at potentials above the discharge potential of the aromatic (2.0 V *vs.* sce) (612). Although cyanide ion is anodically cooxidized to cyano radical at these potentials, the above results do imply that the aromatic must undergo charge transfer. A concerted discharge mechanism involving cyanide ion and aromatic or a route by which anisole cation radical and cyanide radical combine cannot be excluded (445).

A successful approach to cyanation of aromatic compounds has recently been reported by Andreades and Zahnow (14). The method consists in electrolysis (cpe, 2.0 V *vs.* sce) of the aromatic in CH_3CN solution containing $(C_2H_5)_4NCN$ as electrolyte. Cyanation of 1,2- and 1,4-dimethoxybenzenes affords *o*-cyanoanisole and *p*-cyanoanisole, while 1,2,3-trimethoxybenzene results in formation of 2,6-dimethoxybenzonitrile. The unusual ether displacement reactions could be rationalized in terms of a number of mechanisms including one in which two electrons are removed in a concerted manner assisted by approach of cyanide, as depicted for 1,4-dimethoxybenzene in Eq 24. The σ complex could then eliminate the elements of methoxy cation as a proton and formaldehyde.



(Eq 24)

A summary of cyanation of aromatic compounds is given in Table VII.

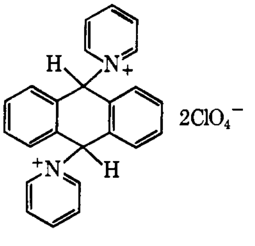
5. Halogenation

Electrochemical halogenation of aromatic compounds has been adequately reviewed (12, 76, 206, 747, 782). To extend the scope of the reaction and limit side reactions observed in aqueous media, future workers should consider use of nonaqueous solutions.

6. Miscellaneous

Anthracene may be dipyridinated in CH_3CN solution to afford a good yield of 9,10-dihydroanthranyldipyridinium diperchlorate (**25**). The reaction is believed to proceed *via* the anthracene dication (511). Of the three possible isomers (9,10-dihydroanthracene is not planar), only one of unknown configuration was isolated. In contrast, oxidation of anthracene in C_2H_5OH–CH_3CN solution appears to proceed by loss of one electron per molecule, giving the dimer bianthrone (**26**) (289).

The formation of N-benzylacetamides by electrooxidation of durene or hexamethylbenzene in CH_3CN is analogous to side-chain acetoxylation (and perhaps methoxylation). The reaction has been described by Eberson and Nyberg as a two-electron transfer from the organic substrate to form the nitrilium salt **27** (Eq 25 and 26) (168). On treatment with water, the salt **27** is hydrolyzed to the N-benzylacetamide (**28**).



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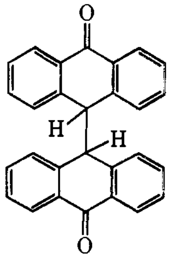


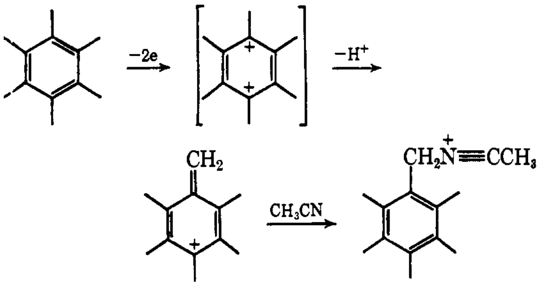
26

Electrolysis of toluene or cumene in anhydrous CH_3CN solution containing perchlorate electrolyte (noncontrolled potential conditions) gives rise to

Table VII

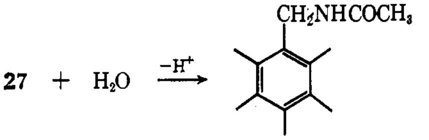
Cyanation of Aromatic Compounds

Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
Toluene (HCN, CH_3OH, NaCN)	Pt	*o*-, *m*-, *p*-Cyanotoluenes $o:m:p = 1:0.2:2.5$ (very low yield)	446
Anisole			
(a) (CH_3CN, $(C_2H_5)_4NCN$), cpe 2.0 V *vs.* sce	Pt	*p*-Cyanoanisole (poor)	14
(b) (HCN, CH_3OH, NaCN)	Pt	*o*- and *p*-Cyanoanisole, $o:p = 38:62$ (3 g/36 gsm)	446, 612
1,4-Dimethoxybenzene (CH_3CN, $(C_2H_5)_4NCN$), cpe 2.0 V *vs.* sce	Pt	*p*-Cyanoanisole (95)	14
1,2-Dimethoxybenzene (CH_3CN, $(C_2H_5)_4NCN$), cpe 2.0 V *vs.* sce	Pt	*o*-Cyanoanisole (94)	14
1,3-Dimethoxybenzene (CH_3CN, $(C_2H_5)_4NCN$), cpe 2.0 V *vs.* sce	Pt	2,4-Dimethoxybenzonitrile	14
1,2,3-Trimethoxybenzene (CH_3CN, $(C_2H_5)_4NCN$)	Pt	2,6-Dimethoxybenzonitrile	14
Tetralin (HCN, CH_3OH, NaCN)	Pt	1-Methoxytetralin (10 g/78 gsm), 6-cyanotetralin (1.3 g)	446, 612
Biphenyl (CH_3CN, $(C_2H_5)_4NCN$)	Pt	4-Cyanobiphenyl	14
Naphthalene (CH_3OH, NaCN)	Pt	1-Cyanonaphthalene	445
Anthracene			
(a) (CH_3OH, NaCN)	Pt	9-Cyanoanthracene	445
(b) (CH_3CN, $(C_2H_5)_4NCN$), cpe 2.0 V *vs.* sce	Pt	9,10-Dicyanoanthracene (54)	14



(Eq 25)

27



(Eq 26)

28

products such as bibenzyls, possibly due to radical abstraction by electrochemically generated perchlorate radical (444a). This reaction is apparently similar to some side-chain methoxylations (section III.A.2) and nitrate radical abstractions (section II.A.3) mentioned earlier.

The common supposition that the primary electrode process in hydrocarbon oxidation involves the formation of dications has been challenged recently (519a, 621). The variation in $E_{1/2}$ values for hydrocarbons previously reported is probably due to differences in rates of voltage change where coupled chemical reactions are dominant. For 9,10-diphenylanthracene electrooxidation in CH_3CN at all scan-rates employed occurs by removal of two electrons in successive one-electron steps separated by about 0.5 V. The first electron is lost with a rate of charge transfer of the order of 1 cm sec^{-1} and results in a relatively stable cation radical (621).

Table VIII lists some relatively stable cation radicals of aromatic compounds obtained under cpe conditions. These species have been studied by Zweig and coworkers (893–896) using cyclic voltammetry which allows an estimate of the stability of the cation radicals by scanning the cyclic voltammogram at varying speeds. In those fluorescent compounds where the cation radical and corresponding anion radical are sufficiently stable, successive electrochemical reduction and oxidation in aprotic solvents results in luminescent emission (electrochemiluminescence) (200, 331). The stability of cation radicals depends on a number of factors including coplanarity, resonance delocalization (aided by electron-donor substituents), and solvent. Methylene chloride (632) and nitrobenzene (519a) have been found to be better solvents than CH_3CN for stabilizing cation radicals.

B. OXIDATION OF OLEFINIC AND ACETYLENIC COMPOUNDS (TABLE IX)

The recent literature exhibits a variety of electrooxidation reactions of simple olefins. Thus compounds such as ethylene and propylene have been converted, often in high yields, to glycols, nitrate esters, epoxides halohydrins, and vinyl acetates. While several of these processes may involve radical intermediates (*e.g.*, in glycol and nitrate ester formation), others proceed by electrochemical generation or regeneration of chemical oxidants such as hypohalite and OSO_4. Fuel-cell oxidation of olefins has been the subject of a detailed review (635). Inefficient cell reactions (those which proceed poorly to CO_2, H_2, and H_2O) could be of considerable interest to the organic electrochemist.

Oxidation of 3,4-dimethoxypropenylbenzene (**29**) in aqueous media leads to 3,4-dimethoxybenzaldehyde and the corresponding acid (213). In CH_3CN solution, the side chain undergoes oxidation again, providing a dimeric perchlorate formulated as **32**, dimethyldiisoeugenol (formed in a nonelectrochemical acid-catalyzed reaction), and traces of 2,3,6,7-tetramethoxyanthraquinone. An oxidation mechanism involving dimerization of cation radicals **30** at the β-carbon atoms of the side chains followed by ring closure of the re-

TABLE VIII

MISCELLANEOUS OXIDATIONS OF AROMATIC COMPOUNDS

Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
		Pyridination	
Naphthalene (C_5H_5N, CH_3CN, $NaClO_4$), cpe 1.4 V *vs.* Ag, Ag^+ (0.1 *N*)	Pt	No oxidation products isolated[a]	511
Anthracene (C_5H_5N, CH_3CN, $NaClO_4$), cpe 0.95 V *vs.* Ag, Ag^+ (0.1 *N*)	Pt	9,10-Dihydroanthranyldipyridinium diperchlorate[b] (45)	511
9,10-Dibromoanthracene (C_5H_5N, acetone, $NaClO_4$), cpe 1.2 V *vs.* Ag, Ag^+ (0.1 *N*)	Pt	(9-Bromo-10-anthryl) pyridinium perchlorate (37)	511
		Amidation	
Durene (CH_3CN, $NaClO_4$), cpe 1.0 V *vs.* sce	Pt	N-Acetyl-2,4,5-trimethylbenzylamine (38)	168
Hexamethylbenzene (CH_3CN, $NaClO_4$), cpe 0.8 V *vs.* sce	Pt	N-Acetylpentamethylbenzylamine (42)	168
		Dimerization	
Anthracene (CH_3CN, C_2H_5OH, $NaClO_4$), cpe 1 V *vs.* Ag, Ag^+	..	Bianthrone	289
		Radical Abstraction	
Toluene (CH_3CN, $AgClO_4$)	Pt	Benzaldehyde, 1,2-diphenylethane,[c] 4,4′-dimethylbiphenyl[c]	444a
Cumene (CH_3CN, $LiClO_4$, NH_4ClO_4, or $AgClO_4$)	Pt	2-Phenyl-2-propanol,[c] acetophenone, 2,3-dimethyl-2,3-diphenylbutane, 4,4′-diisopropylbiphenyl, 2-(*p*-isopropylphenyl)-2-phenylpropane, 2-(isopropylphenyl)-2-phenylpropanes	444a
		Some Relatively Stable Cation Radicals	
Methoxybenzenes (CH_3CN, $(n\text{-}C_3H_7)_4NClO_4$), cpe	Pt	Corresponding cation radicals[d]	889
9,10-Diphenylanthracene			
(a) (CH_3CN, $(C_2H_5)_4NClO_4$), cpe 1.5 V *vs.* sce	Pt	Cation radical[d,e]	621, 721, 812
(b) CH_2Cl_2, $(n\text{-}C_4H_9)_4NClO_4$), cpe	Pt	Cation radical[d,f]	632
Rubrene			
(a) (DMF, $(n\text{-}C_4H_9)_4NClO_4$), cpe 1.0 V *vs.* sce	Pt	Cation radical[e,f]	349a, 521, 812
(b) (CH_2Cl_2, $(n\text{-}C_4H_9)_4NClO_4$), cpe	Pt	Cation radical[d,f]	632
Methoxy- and methylthionaphthalenes (CH_3CN, $(n\text{-}C_4H_9)_4NClO_4$), cpe	Pt	Corresponding cation radicals[e,f]	894
Methoxy-, methylthio-, and phenoxyanthracenes (CH_3CN, $(n\text{-}C_4H_9)_4NClO_4$), cpe	Pt	Corresponding cation radicals[e,f]	894
Methoxy- and methylthiobiphenyls (CH_3CN, $(n\text{-}C_4H_9)_4NClO_4$)	Pt	Corresponding cation radicals[e,f]	894
1,5-Dimethoxy-4,8-diphenoxynaphthalene 9,10-Bis(phenylethynyl)anthracene 10,10′-Dimethoxy-9,9′-bianthracenyl 1,6-Dimethoxypyrene 1,6-Bis(methylthio)pyrene } (CH_3CN, $(n\text{-}C_4H_9)_4NClO_4$), cpe	Pt	Corresponding cation radicals[e,f]	894
1,3,4,7-Tetraphenylisobenzofuran (DMF, $(n\text{-}C_4H_9)_4NClO_4$), cpe 0.98 V *vs.* sce	Pt	Cation radical[e,f]	895
1,3-Bis-*p*-anisyl-4,7-diphenylisobenzofuran (DMF, $(n\text{-}C_4H_9)_4NClO_4$)	Pt	Cation radical[e,f]	895
1,3,6,8-Tetraphenylpyrene (CH_2Cl_2, $(n\text{-}C_4H_9)_4NClO_4$), cpe	Pt	Cation radical[d,f]	632
Tetracene (CH_2Cl_2, $(n\text{-}C_4H_9)_4NClO_4$), cpe	Pt	Cation radical[d,f]	632

[a] Film formed on the anode inhibiting further reaction. [b] A single isomer. [c] Major products. [d] Esr spectrum observed. [e] Electrochemiluminescence observed. [f] Observed by cyclic voltammetry.

sultant dication **31** and ejection of hydrogen ion has been proposed to account for the experimental results (Eq 27) (595).

In contrast, in CH_3CN solution containing pyridine, **29** is oxidized by a two-electron process to give the dipyridinium diperchlorate **33** in nearly quantitative yield and current efficiency. The authors propose that pyridine participates in the electrode reaction by decreasing the energy required to remove a second electron from **29**. The oxidation is depicted as a concerted push–pull attack of the unshared electron pair of pyridine and the positive anode surface.

Methoxylation of *cis*- and *trans*-stilbene in CH_3OH containing $NaOCH_3$ as electrolyte affords *meso*- and *dl*-hydrobenzoin dimethyl ether (367, 368). The ratio of *meso* to *dl* in each case indicates a preference for *cis* methoxylation. The reaction mechanism has been described as proceeding through the radical cation of stilbene oriented planar to the anode surface. Solvent attack on the cationic species (rather than addition of adsorbed methoxy radicals to the olefin) then occurs (627). The course of the reaction is drastically altered when NH_4ClO_4 or NH_4Br is used as electrolyte. In an unusual reaction the former electrolyte gives benzaldehyde as the main product, while the latter affords the dibromide as the main product, along with α-methoxy-β-bromo-1,2-diphenylethane and a small quantity of *meso*-hydrobenzoin dimethyl ether.

TABLE IX

OXIDATION OF OLEFINIC AND ACETYLENIC COMPOUNDS

Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
		Hydroxylation (Oxidation in Aqueous Media)	
Ethylene			
(a) (H_2O, NaOH or H_2SO_4)	Fe, Pt	Ethylene glycol	362, 529, 871
(b) (H_2O, Na_2SO_4), cpe 0.4 V *vs.* sce	Pd	Acetaldehyde	754
(c) (H_2O, NaCl, pH 10.6)	C	Ethylene oxide (48), ethylene dichloride (2)	407, 408, 478, 648
(d) (H_2O, chloride)	C	Ethylene chlorohydrin, ethylene dichloride, ethylene glycol	46, 333, 399, 527, 528, 530, 870
(e) (HOAc, LiOAc, Pd)	C	Vinyl acetate	869
Propylene			
(a) (H_2O, NaCl, pH 11)	C	Propylene oxide (93), propylene dichloride (2)	478
(b) (H_2O, OsO_4, $K_3Fe(CN)_6$)	Pt	Propylene glycol	524
(c) (HOAc, LiOAc, Pd)	C	Propenyl acetate	869
Allyl alcohol (H_2O, NaCl or HCl)	C	Glycerol chlorohydrin	771, 772
Acetylene			
(a) (H_2O, $HgSO_4$)	Hg	Acetaldehyde	99, 100, 742
(b) (H_2O, KOH)	Pt	Potassium formate	121
(c) (H_2O, H_2SO_4)	Pt	Acetic acid	39, 121
2-Methyl-2-butene (H_2O, H_2SO_4, KI)	Pt	Methyl isopropyl ketone, iodo-substituted ketones	357
Oleic acid (H_2O, acetone, H_2SO_4)	Pt	Dihydroxystearic acid	519
Mixture of 1- and 2-*n*-butenes (H_2O, H_2SO_4)	Pt	Methyl ethyl ketone (92)	854
2-Vinylpyridine (H_2O)	. . .	2-Pyridylethylene glycol (6), 2-pyridinecarboxaldehyde	201
Cyclohexene			
(a) (H_2O, H_2SO_4)	PbO_2	1,2-Cyclohexanediol, cyclohexanone, adipic acid, tartaric acid, malonic acid, CO_2, CO	862
(b) (H_2O, $NaHCO_3$)	PbO_2	Cyclohexen-1-one-3 (15.5 g/74 gsm), polymer (27.4 g)	657
Cyclooctatetraene (H_2O, HOAc, H_2SO_4)	. . .	Phenylacetaldehyde (79)	576
Isoeugenol (H_2O, H_2SO_4)	PbO_2	Vanillin (trace), resin	507
Potassium isoeugenol sulfonate (H_2O, Na_2CO_3)	PbO_2	Vanillin (50), vanillic acid (4.3), divanillic acid (20.5)	213, 241
Indigo			
(a) (H_2O, H_2SO_4)	C	Isatin (0.7 g/5.24 gsm)	214
(b) (H_2O, HCl)	Pt	Mono- and dichloroisatin, 2,4,6-trichloroaniline	214
(c) (H_2O, HBr)	C	5,5'-Dibromoindigo, 5-bromoisatin, 2,4,6-tribromoaniline	214
α-Pinene (H_2O, H_2SO_4)	Pt, PbO_2	Cymene,[a] dipentene,[a] terebic acid, *cis*-terpin,[a] α-terpineol,[a] polymer	246, 657
β-Pinene (H_2O, H_2SO_4)	Pt, PbO_2	Cymene,[a] dipentene,[a] cineol,[a] α-terpineol,[a] *cis*-terpin,[a] terebic acid, α-pinene,[a] polymer	657
3,4-Dimethoxypropenylbenzene (H_2O, KOH)	PbO_2	3,4-Dimethoxybenzaldehyde (77.8), 3,4-dimethoxybenzoic acid (12.7)	213
p-Propenylanisole (H_2O, Na_2SO_4)	PbO_2	Anisaldehyde (52), anisic acid (25.4)	213
		Alkoxylation	
Ethylene (CH_3OH, KOH)	Pt	No alkoxylation	827
1,3-Cyclohexadiene (CH_3OH, KOH)	Pt	Mixture of 1,2- and 1,4-dimethoxycyclohexenes (9)	826
1,4-Cyclohexadiene (CH_3OH, KOH)	Pt	No alkoxylation product	826
Isoprene (CH_3OH, KOH)	Pt	Polymer	826
1,4-Diphenylbutadiene (CH_3OH, KOH), cpe 1.55 V *vs.* sce	Pt	*trans*-1,4-Dimethoxy-1,4-diphenyl-2-butene (60)	827
5,5,6,6-Tetramethoxy-1,3-cyclohexadiene (CH_3OH, KOH)	Pt	Hexamethyl *cis,cis*-orthomuconate (77)	41
trans-Stilbene			
(a) (CH_3OH, $NaOCH_3$)	Pt	Hydrobenzoin dimethyl ether (*meso* (20); *dl* (44)), bibenzyl (trace)	367, 368
(b) (CH_3OH, NH_4Br)	Pt	*erythro*-Stilbene dibromide (2.8 g/5 gsm), α-methoxy-β-bromo-1,2-diphenylethane (1.4 g), *meso*-hydrobenzoin dimethyl ether (trace)	368
(c) (CH_3OH, NH_4ClO_4)	Pt	Benzaldehyde (2.5 g/5 gsm), HCHO	368
cis-Stilbene (CH_3OH, $NaOCH_3$)	Pt	Hydrobenzoin dimethyl ether (*meso*- (26); *dl*-(18)), bibenzyl (7)	367, 368
Styrene			
(a) (CH_3OH, $NaOCH_3$)	Pt	Styrene glycol dimethyl ether (16 g/50 gsm), α-methoxyethylbenzene (0.9 g), β-methoxyethylbenzene (trace), *meso*-1,4-dimethoxy-2,3-diphenylbutane (0.7 g), HCHO	371
(b) (C_2H_5OH, $NaOC_2H_5$)	Pt	Styrene glycol diethyl ether (6.5 g/52 gsm), *meso*-1,4-diethoxy-2,3-diphenylbutane (1.5 g), polymeric material (4.5 g)	368
α-Methylstyrene (CH_3OH, $NaOCH_3$)	Pt	1-Phenyl-1-methylethylene glycol dimethyl ether (13.7 g/59 gsm), α-methoxyisopropylbenzene (2.2 g), acetophenone (3.2 g), β-methoxyisopropylbenzene (trace)	371
1,1-Diphenylethylene (CH_3OH, $NaOCH_3$)	Pt	1,1-Diphenylethylene glycol dimethyl ether (13.8 g/45 gsm)	371

Table IX (*Continued*)

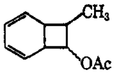
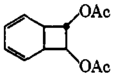
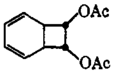
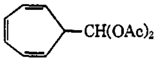
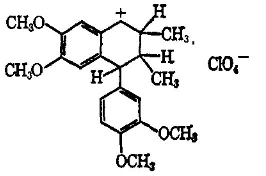
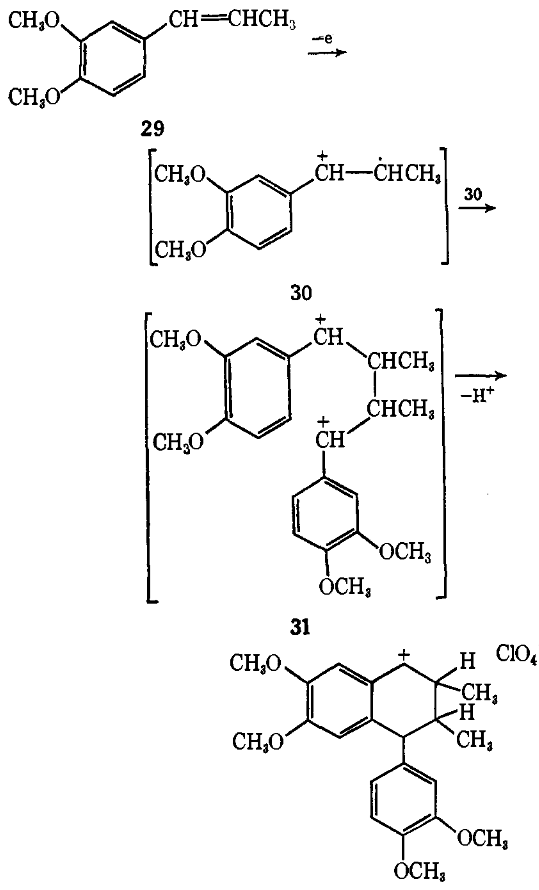
Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
Norbornene (CH_3OH, $NaOCH_3$)	Pt	*exo,syn*-2,7-Dimethoxybicyclo[2.2.1]heptane (1.7 g/14.1 gsm), *exo*-2-methoxybicyclo[2.2.1]heptane (1.0 g), two unidentified ethers (1.1 g)	368
Cinnamic acid (CH_3OH, NH_4Cl)	Pt, C	1-Chloro-2-methoxy-2-phenylpropionic acid (50)	479
Cinnamic acid (CH_3OH, NH_4Br)	Pt, C	1-Bromo-2-methoxy-2-phenylpropionic adid (40)	479
		Acetoxylation	
2-Methyl-2-butene (HOAc, NaOAc)	Pt	2-Methyl-3-acetoxybutene (50), 2,2-dimethyl-3-acetoxybutane (10), 2-methyl-3-acetoxybutane (4)	137
3-Methylpentene-2 (HOAc, NaOAc)	Pt	3-Methyl-4-acetoxy-2-pentene (30), 2-ethyl-3-acetoxybutene (30)	137
trans-Stilbene			
(a) (HOAc, NaOAc)	Pt	*meso*-1,2-Di-O-acetyl-1,2-diphenylethylene glycol,[b] *threo*-1-O-acetyl-1,2-diphenylethylene glycol, *erythro*-1,2-diphenyl-1-propyl acetate	515
(b) (H_2O, HOAc, NaOAc)	Pt	*dl*-1,2-Di-O-acetyl-1,2-diphenylethylene glycol, *threo*-1-O-acetyl-1,2-diphenylethylene glycol,[b] *erythro*- and *threo*-1,2-diphenyl-1-propyl acetates	515
Diphenylacetylene (HOAc, Ac_2O, KOAc)	C	Benzil (28),[c] benzoin acetate (4), α,α'-stilbenediol diacetate (trace)	436
1,1-Diphenylethylene (HOAc, NaOAc), cpe 1.50 V *vs.* sce	Pt	1,2-Di-O-acetyl-1,1-diphenylethylene glycol (15), 2-O-acetyl-1,1-diphenylethylene glycol (59)	167, 515
Cyclooctatetraene			
(a) (HOAc, NaOAc), cpe 1.50 V *vs.* sce	Pt	 (7.7) A  B  C  (34.7) A:B:C = 27:44:29	169
(b) (HOAc, KOAc)[d]	C	A:B:C = 34–44:28–33:28–33; no methylation product	169
		Carbomethoxylation	
Styrene (CH_3OH, $NaOCH_3$, CO)	Pt	Methyl *trans*-cinnamate (14), methyl β-methoxy-β-phenylpropionate (3.6), methyl β-phenylpropionate (3.1), dimethyl *meso*-β,γ-diphenyladipate (trace), styrene glycol dimethyl ether (5.6), styrene (57)	373, 374
α-Methylstyrene (CH_3OH, $NaOCH_3$, CO)	Pt	Methyl *trans*-β-methylcinnamate (14.8), methyl 3-phenyl-3-butenoate (4.9), methyl β-methyl-β-phenylpropionate (1), α-methylstyrene glycol dimethyl ether (2.2)	373, 374
1,1-Diphenylethylene (CH_3OH, $NaOCH_3$, CO)	Pt	Methyl β-phenylcinnamate (30), 1,1-diphenylethylene glycol dimethyl ether (25)	373, 374
		Cyanation	
Butadiene			
(a) (Liq NH_3, CuCN)	Pt	No cyanation product	445
(b) (CH_3OH, HCN, NaCN)	Pt	Four unidentified products	445
Cyclohexene			
(a) (CH_3OH, $Hg(CN)_2$)	Pt	Hg,[b] HCHO, HCN,[b] cyclohexyl cyanide, 3-cyanocyclohexene, 3,3'-bicyclohexenyl[b]	868
(b) (CH_3CN, CuCN, or AgCN)	Pt	No cyanation product	445
1,3-Cyclohexadiene (C_5H_5N, AgCN)	Pt, Ta	No cyanation product	699
		Miscellaneous	
Ethylene (HOAc, acetone, $Ca(NO_3)_2$)	Pt	Ethylene glycol dinitrate, tetramethylene glycol dinitrate (total yield: 1.88 g/A hr)	598, 599
Crotonic acid (HOAc, acetone, $Ca(NO_3)_2$)	Pt	Nitric acid esters (2.8 g/A hr)	598
Methylpentadiene (HOAc, acetone, $Ca(NO_3)_2$)	Pt	Nitric acid esters (3.7 g/A hr)	598
Methylcyclopentadiene dimer (DMF, CO, $MnCl_2$, $Fe(CO)_5$)	Mn	Methylcyclopentadienylmanganese tricarbonyl (7)	192
Indene (dicyclohexylamine, CO, $Mn(OAc)_2$, LiBr, $Co(CO)_5$)	Mn	Indenylmanganese tricarbonyl (good)	192
Fluorene (hexamethyl phosphoramide, CO, $MnCl_2$, $Cr(CO)_6$)	Mn	Fluorenylmanganese tricarbonyl (excellent)	192
Phenylcyclopentadiene (DMF, CO, MnI_2, $Fe(CO)_5$)	Mn	Phenylcyclopentadienylmanganese tricarbonyl	192

TABLE IX (*Continued*)

Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
1,4-Cyclohexadiene (CH_3CN, $LiClO_4$), cpe 1.6 V *vs.* sce	Pt	Benzene	306
Cycloheptatriene (CH_3CN, $LiClO_4$), cpe 1.5 V *vs.* Ag, Ag^+	Pt	Tropylium perchlorate (quant)	306
Bitropyl (CH_3CN, $LiClO_4$), cpe 1.03 V *vs.* Ag, Ag^+	Pt	Tropylium perchlorate (quant)	306
Bicyclo[2.2.1]- and bicyclo[3.2.0]hepta-2,5-diene, electrolytically inert under reaction conditions			306
3,4-Dimethoxypropenylbenzene			
(a) (CH_3CN, C_5H_5N, $NaClO_4$), cpe 1.2 V *vs.* sce	Pt	3,4-Dimethoxypropenylbenzene dipyridinium diperchlorate (95)	595
(b) (CH_3CN, $NaClO_4$), cpe 0.98 V *vs.* sce	Pt	Dimethyldiisoeugenol[a]  2,3,6,7-tetramethoxyanthraquinone (trace)	595
Cyclohexene (CH_3CN, AgF)	Pt	1,2-Difluorocyclohexane	700
1,1-Diphenylethylene (CH_3CN, AgF)	Pt	1,2-Difluoro-1,1-diphenylethane	700
Tetrakis(dimethylamino)ethylene (TDE)			
(a) (CH_3CN, Et_4NClO_4), cpe −0.7 V *vs.* sce	Hg	TDE cation radical	461
(b) (CH_3CN, Et_4NClO_4), cpe −0.6 V *vs.* sce	Hg	TDE dication	461
(c) (DMF or CH_3CN, Et_4NBr), cpe −0.1 V *vs.* sce	Hg	Tetrakis(dimethylamino)ethylene dibromide (TDE^{2+}-$(Br^-)_2$)	461
(d) (DMF or CH_3CN, Et_4NClO_4) cpe −0.1 V *vs.* sce	Hg	$TDE^{2+}(ClO_4^-)_2$	461

[a] Nonelectrochemical product. [b] Major product. [c] Per cent gas chromatographic peak area. [d] Constant current electrolysis.



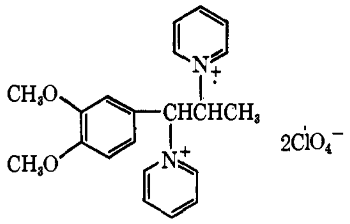
29

30

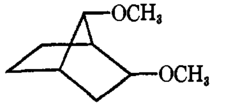
31

32

(Eq 27)


33

Methoxylation of norbornene under basic conditions results in the rearranged product **34** and *exo*-methoxybicyclo[2.2.1]heptane (**35**) (368). No *cis*-2,3-dimethoxybicyclo[2.2.1]heptane could be found. The mechanism has been pictured as a methoxy radical attack on the olefin, subsequent electrooxidation, rearrangement, and attack by methoxide ion to give **34**. An alternative route involving norbornene cation radical could readily account for the products.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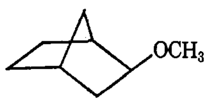
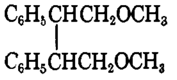

35

Methoxylation of 1,3-cyclohexadiene provides a mixture of 1,2- and 1,4-dimethoxycyclohexenes (826). In contrast 1,4-diphenylbutadiene affords the 1,4-addition product (827), while 5,5,6,6-tetramethoxy-1,3-cyclohexadiene undergoes ring cleavage to hexamethyl *cis,cis*-orthomuconate (see section III.A.2).

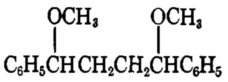
These reactions may be rationalized in terms of benzylic and allylic cation radical intermediates.

In addition to styrene glycol dimethyl ether, the methoxylation of styrene gives a small quantity of *meso*-1,4-dimethoxy-2,3-diphenylbutane (**36**) and no 1,4-dimethoxy-1,4-diphenylbutane (**37**). Formation of **36** suggests that the rate of reaction of styrene cation radical **38** with solvent is greater than the rate of dimerization. The product **36** then derives from the benzilically stabilized radical intermediate **39** (Eq 28) (372).



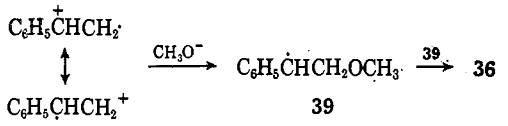
$C_6H_5CHCH_2OCH_3$ | $C_6H_5CHCH_2OCH_3$

36



$C_6H_5CH(OCH_3)CH_2CH_2CH(OCH_3)C_6H_5$

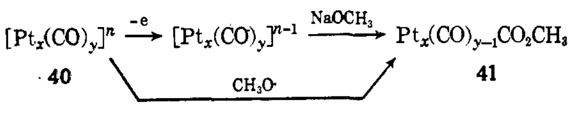
37



$C_6H_5\overset{+}{C}HCH_2\cdot \leftrightarrow C_6H_5\dot{C}HCH_2^+ \xrightarrow{CH_3O^-} C_6H_5\dot{C}HCH_2OCH_3 \xrightarrow{39} 36$ (Eq 28)

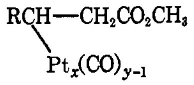
38 **39**

In the electrolysis of a basic CH_3OH–carbon monoxide solution at Pt electrodes, the cathode dissolves to give an isolatable platinum–carbonyl complex **40**. Electrooxidation of suitable olefins in presence of this complex provides a novel synthesis of α,β-unsaturated carboxylic esters. The reaction is believed to proceed by methoxy radical attack on **40**, or direct oxidation of **40** to give a carbomethoxyplatinum carbonylate (**41**) (Eq 29). This new complex adds a carbomethoxy group to the olefin, presumably *via* formation of a σ metal–carbon bond as in **42**, followed by decomposition to the observed product (373, 374).



$[Pt_x(CO)_y]^n \xrightarrow{-e} [Pt_x(CO)_y]^{n-1} \xrightarrow{NaOCH_3} Pt_x(CO)_{y-1}CO_2CH_3$; **40** $\xrightarrow{CH_3O\cdot}$ **41**

40 **41**



$RCH(Pt_x(CO)_{y-1})—CH_2CO_2CH_3$

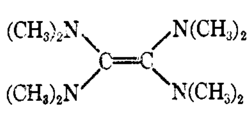
42 (Eq 29)

Acetoxylation of olefins has been reviewed by Eberson (161).

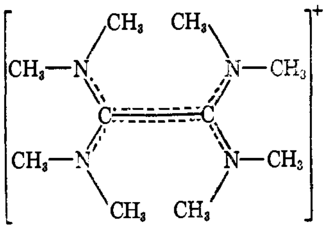
Cyanation of olefins or dienes by a number of methods has thus far been relatively unsuccessful.

The oxidation of cycloheptatriene or bitropyl under cpe conditions has been shown by Geske to proceed by a stepwise two-electron oxidation to afford tropylium perchlorate in nearly quantitative yield (306).

Polarography of tetrakis(dimethylamino)ethylene (**43**) in aprotic media results in a two-step wave corresponding to oxidation to the cation radical **44** and the corresponding dication. This remarkably stable radical bears some resemblance to the cation radical of N,N,N′,N′-tetramethylphenylenediamine and has been considered to possess the estimated structure shown below in which restricted rotation exists about the C–$N(CH_3)_2$ bond (461).



43



44

C. OXIDATION OF AMINES, AMINO ACIDS, AND QUATERNARY AMMONIUM SALTS (TABLE X)

1. *Aliphatic Amines*

The electrochemical oxidation (cpe) of primary and secondary aliphatic amines in CH_3CN has been examined by Barnes and Mann (32). At least half of the amine is recovered in the unreactive protonated form. Other products include varying quantities of ammonium perchlorate, aldehyde, nitrogen, and hydrocarbon. Controlled-potential coulometry indicates that from 0.71 to 0.87 electron is transferred per molecule of amine. Amines bearing hydrogens α to nitrogen are found generally to produce aldehydes. *t*-Butylamine, lacking these hydrogens, is converted to *t*-butyl alcohol. A dual mechanism has been suggested on the basis of cyclic voltammetry and cpe with one sequence of reactions predominating at low potentials, the other at high potentials. The low-potential course (route A, Eq 30–34 and 37) involves a one-electron transfer to form a cation radical (**45**) which almost entirely decomposes to a carbonium ion and amidogen radical. At higher potentials (route B, Eq 30 and 35–37), two electrons and a proton are lost and an iminium salt (**46**) is formed which may hydrolyze to aldehyde and ammonia. The relative importance of the two pathways is dependent on the applied potential and the molecular structure of the amine. Route B bears some resemblance to the mechanism suggested for oxidation of primary amines in alkaline permanganate solution (825).

Route A

$$RCH_2NH_2 \rightarrow \underset{\mathbf{45}}{RCH_2\overset{+}{\dot{N}}H_2} + e \qquad \text{(Eq 30)}$$

$$\mathbf{45} \rightarrow R\overset{+}{C}H_2 + \cdot NH_2 \qquad \text{(Eq 31)}$$

$$R\overset{+}{C}H_2 \rightarrow H^+ + \text{hydrocarbons} \qquad \text{(Eq 32)}$$

$$R\overset{+}{C}H_2 + CH_3CN \rightarrow H^+ + \text{carbonium ion condensation products} \qquad \text{(Eq 33)}$$

$$\cdot NH_2 \rightarrow 0.25N_2 + 0.5NH_3 + 0.5H^+ + 0.5e \qquad \text{(Eq 34)}$$

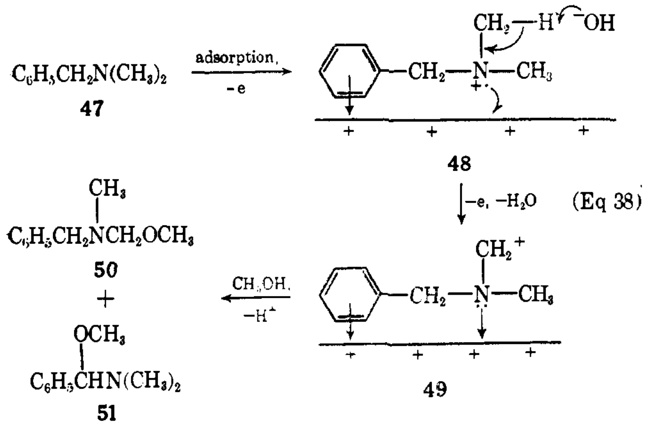
Route B

$$\mathbf{45} \rightleftharpoons R\dot{C}HNH_2 + H^+ \qquad \text{(Eq 35)}$$

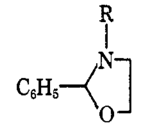
$$R\dot{C}HNH_2 \xrightarrow{-e} \underset{\mathbf{46}}{RCH{=}NH_2^+} \xrightarrow[+H_2O]{-H^+,} RCHO + NH_3 \qquad \text{(Eq 36)}$$

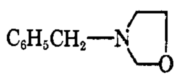
$$NH_3 \rightarrow 0.5N_2 + 3H^+ + 3e \qquad \text{(Eq 37)}$$

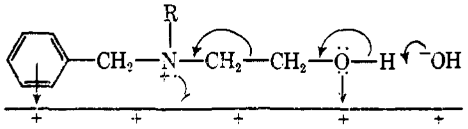
The oxidation of triethylamine in CH_3CN or DMSO affords triethylammonium ion resulting from hydrogen-atom abstraction from solvent by triethylamine cation radical (140, 684). In methanolic solution (KOH electrolyte), N,N-dimethylbenzylamine (**47**) gives the methoxymethylamine **50** and methoxybenzylamine **51** in a ratio of 4:1, respectively (831). To account for an unusual preponderance of **50**, the reaction mechanism has been depicted in terms of the adsorbed cation radical **48**. This could undergo a base-assisted concerted deprotonation and electron transfer giving rise to the resonance-stabilized cation **49**. A proton would be lost from the methyl rather than the benzyl group in **48** because of the relative availability of protons at the former position. The primary cation **49** would thus be formed remotely from the anode plane. The alternative deprotonation at the benzylic position would entail the relatively unfavorable generation of a positive center closer to the anode surface and adjacent to an already positively polarized aromatic ring. Recent studies of the chemical oxidation of N,N-dialkylbenzylamines with nitrous acid and with chlorine dioxide in aqueous media have demonstrated that cleavage occurs predominantly at the N-alkyl rather than at the N-benzyl position (676, 728). The nitrous acid reaction has been described in terms of a process involving a cyclic transition state. Such a mechanism which accounts for N-alkyl cleavage on steric grounds has some analogy to the above electrochemical methoxylation. In contrast oxidation of **47** with N-bromosuccinimide, manganese dioxide, benzoyl peroxide, or alkaline potassium permanganate affords benzaldehyde (80, 138, 158, 741).



In general, amino functions are somewhat resistant to oxidation in acidic media due to protonation. As a result amino alcohols are oxidized to the corresponding amino acids. In basic media, however, the situation is quite different; N-benzyl-N-methylethanolamine in methanolic solution (containing KOH) gives a mixture of three products in approximately equal yield: N-methoxymethyl-N-methylbenzylamine (**50**), 3-methyl-2-phenyloxazolidine (**52**), and 3-benzyloxazolidine (**53**). Oxidation of N-benzyldiethanolamine affords **53** and 3-(β-hydroxyethyl)-2-phenyloxazolidine (**54**) (831).


52, R = CH_3
54, R = CH_2CH_2OH


53


55

A mechanism similar to Eq 38 readily accounts for the intramolecular cyclizations of the above amino alcohols. In a competing process concerted transfer of an electron to the anode from the cation radical **55** of the adsorbed N-benzyl-N-alkylethanolamines may be accompanied by loss of the elements of formaldehyde and a proton to afford the dehydroxymethylation products **50** and **53**. Intramolecular cyclization of ethanolamines has been observed previously in homogeneous solution using mercuric acetate–ethylenediaminetetraacetic acid reagent (564).

Aldehydes, which are the primary products, have been obtained in good yield from electrooxidation of amino acids in acid solution provided that these products are removed as quickly as possible to prevent their further oxidation (764). Similar products have been observed by the action of hydrogen peroxide solutions on amino acids (225).

2. *Aromatic Amines*

The electrochemical polymerization of aniline has been the subject of a number of investigations. One of the earliest reports constitutes one of the first examples of electrolysis of an organic fused salt: aniline hydrochloride at 160° to afford aniline black, induline, and azophenine (749). Recently, Mohilner, Adams, and Argersinger have shown that the initial charge transfer for aniline oxidation in aqueous acid occurs by loss of two electrons (563). This step is second order with respect to aniline. In addition, since *p*-aminodiphenylamine (**56**) is a likely intermediate in the formation of emeraldine (**57**) (one of the constituents of aniline black), these workers have proposed a *head-to-*

TABLE X

OXIDATION OF AMINES, AMINO ACIDS, AND QUATERNARY AMMONIUM SALTS

Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
Aliphatic Amines and Amino Alcohols			
Methylamine			
(a) (LiCl or $LiNHCH_3$)	Pt	1,3,5-Trimethylhexahydro-*s*-triazine, N-methylformamide	43
(b) (CH_3CN, $NaClO_4$),[a] cpe 1.2 V *vs.* Ag, Ag^+ (0.1 M)	Pt	HCHO (3), NH_4ClO_4 (22), N_2 (25), CH_4	32
n-Propylamine (CH_3CN, $NaClO_4$),[a] cpe 1.2 V *vs.* Ag, Ag^+ (0.1 M)	Pt	2-Methyl-2-pentenalpropylamine (4), NH_4ClO_4 (14), N_2 (22), C_1–C_3 hydrocarbons (CH_4 predominates)	32
Allylamine (CH_3CN, $NaClO_4$),[a] cpe 2.0 V *vs.* Ag, Ag^+ (0.1 M)	Pt	Acrolein (14), NH_4ClO_4 (18), N_2, C_1–C_3 hydrocarbons	32
n-Butylamine (CH_3CN, $NaClO_4$),[a] cpe 1.2 V *vs.* Ag, Ag^+ (0.1 M)	Pt	*n*-Butyraldehyde (3), NH_4ClO_4 (11), N_2, C_1–C_4 hydrocarbons	32
Isobutylamine (CH_3CN, $NaClO_4$),[a] cpe 1.2 V *vs.* Ag, Ag^+ (0.1 M)	Pt	NH_4ClO_4 (14), N_2 (20), C_1–C_4 hydrocarbons (isobutylene and propylene predominate)	32
t-Butylamine (CH_3CN, $NaClO_4$),[a] cpe 1.2 V *vs.* Ag, Ag^+ (0.1 M)	Pt	*t*-Butyl alcohol (4), NH_4ClO_4 (25), N_2, C_1–C_4 hydrocarbons (isobutylene predominates)	32
Hexylamine (CH_3CN, $NaClO_4$),[a] cpe 1.4 V *vs.* Ag, Ag^+ (0.1 M)	Pt	Caproaldehyde (3), NH_4ClO_4 (19), N_2 (25), C_1–C_6 hydrocarbons (ethylene predominates)	32
Cyclohexylamine (CH_3CN, $NaClO_4$),[a] cpe 1.4 V *vs.* Ag, Ag^+ (0.1 M)	Pt	Aldehyde (3), NH_4ClO_4 (15), N_2 (17), cyclohexene (trace)	32
Benzylamine (CH_3CN, $NaClO_4$), cpe 1.5 V *vs.* Ag, Ag^+ (0.1 M)	Pt	Benzaldehyde (15), NH_4ClO_4 (5), N_2	32
Triethylamine			
(a) (DMSO, $Pb(NO_3)_2$), cpe 1.70 V *vs.* Pb, Pb^{2+}	Pt	Triethylammonium nitrate (80)	140
(b) (CH_3CN, $NaClO_4$)	Pt	Triethylammonium perchlorate (90–95)	684
N,N-Dimethylbenzylamine (CH_3OH, KOH)	Pt	N,N-Dimethyl-α-methoxybenzylamine, N-methoxymethyl-N-methylbenzylamine (ratio 1:4, respectively)	831
Piperidine (H_2O, H_2SO_4)	PbO_2	δ-Aminovaleric acid, δ-aminovaleraldehyde, glutaric acid, succinic acid, HCO_2H, NH_3, CO_2, CO	865
Ethanolamine (H_2O, H_2SO_4)	Pt, PbO_2	Glycine (39–66)	558
β-Amino-*n*-propyl alcohol (H_2O, H_2SO_4)	Pt, PbO_2	α-Alanine (39–45)	558
γ-Amino-*n*-propyl alcohol (H_2O, H_2SO_4)	Pt, PbO_2	β-Alanine (64–80)	558, 670
β-Aminobutyl alcohol (H_2O, H_2SO_4)	PbO_2	α-Aminobutyric acid (49)	558, 561
β-Aminoisobutyl alcohol (H_2O, H_2SO_4)	PbO_2	α-Aminoisobutyric acid (31)	558, 561
δ-Amino-*n*-butyl alcohol (H_2O, H_2SO_4)	PbO_2	γ-Aminobutyric acid	562
ϵ-Amino-*n*-amyl alcohol (H_2O, H_2SO_4)	Pt, PbO_2	δ-Aminovaleric acid (31–59)	558
N-Benzyl-N-methylethanolamine (CH_3OH, KOH)	Pt	3-Methyl-2-phenyloxazolidine, 3-benzyloxazolidine, N-methoxymethyl-N-methylbenzylamine (proportion 1:1:1)	831
N-Benzyldiethanolamine (CH_3OH, KOH)	Pt	3-Benzyloxazolidine, 3-(β-hydroxyethyl)-2-phenyloxazolidine	831
Tropine (H_2O, H_2SO_4)	PbO_2	Tropinone	542
Amino Acids			
Glycine			
(a) (H_2O, H_2SO_4)[c]	Pt, PbO_2	HCHO (16.6), HCO_2H (4.9), NH_3, CO_2, amines[b]	225, 247, 487, 764
(b) (H_2O, HNO_3)	PbO_2	Oxalic acid (34)	769
Iminodiacetic acid (H_2O, sodium salt of acid)	Pt	NH_3 (1.4 g/faraday), CO_2 (14.8 g)	247
Methyliminodiacetic acid (H_2O, sodium salt of acid)	Pt	CH_3NH_2, NH_3, CO_2 (14.9 g/faraday)	247
α-Alanine			
(a) (H_2O, H_2SO_4)[c]	PbO_2	Acetaldehyde (36.5), HOAc (17.8), NH_3, HCHO, CO_2, HCO_2H	225, 764
(b) (HNO_3)[c]	PbO_2	HCHO, oxalic acid (27)	769
β-Alanine (H_2O, H_2SO_4)	Pt	NH_3 (1.8 g/faraday), CO_2 (6.8 g), HOAc, HCO_2H	247
α-Aminoisobutyric acid (H_2O, H_2SO_4)	Pt	Acetone, NH_3, CO_2	247
γ-Aminobutyric acid (H_2O, H_2SO_4)	PbO_2	Succinic acid (6)	560, 762
Valine (H_2O, H_2SO_4)[c]	PbO_2	Isobutyraldehyde (32.1), isobutyric acid (27.5)	764
δ-Aminovaleric acid (H_2O, H_2SO_4)	PbO_2	Succinic acid (12.9)	560
Leucine			
(a) (H_2O, H_2SO_4)	Pt, PbO_2	Isovaleraldehyde (0.031 g/4.17 gsm), isovaleric acid (0.11 g), isobutyric acid (0.076 g), acetone (0.094 g), HOAc (0.059 g), HCO_2H (0.11 g), NH_3 (0.10 g), CO_2 (0.65 g)	225, 550, 758, 761
(b) (H_2O, H_2SO_4)[c]	PbO_2	Isovaleraldehyde (53–56), isovaleric acid (20–22)	764
(c) (H_2O, Na_2SO_4 or $(NH_4)_2SO_4$)	PbO_2	Isovaleronitrile (30), CO_2	550
ϵ-Aminocaproic acid (H_2O, H_2SO_4)	PbO_2	Succinic acid (6)	560
Aspartic acid (H_2O, H_2SO_4)	PbO_2	Malonic acid (1.4), HCO_2H (10.8), succinic acid, NH_3, CO_2	761, 767
Glutamic acid (H_2O, HNO_3)	Pt, PbO_2,	Succinic acid (8.7), oxalic acid (8.4), succinimide, HOAc, NH_3, CO_2	755, 769

TABLE X (*Continued*)

Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
Serine (H_2O, $CuCO_3$)	Pt	Glycolaldehyde, NH_3, CO_2	585, 587, 589
Isoserine (H_2O, $CuCO_3$)	Pt	Aminoacetaldehyde[t]	587, 589
Arginine (H_2O, H_2SO_4)	PbO_2	Guanidine (32), succinic acid	757
Cysteine (H_2O, $HClO_4$)	Pt[r]	Cystine	444
Phenylalanine			
(a) (H_2O, H_2SO_4)	PbO_2	NH_3, CO_2	759, 761
(b) (H_2O, HNO_3)	Pt	*p*-Nitrobenzoic acid, benzoic acid, oxalic acid, benzaldehyde	765, 766
p-Nitrophenylalanine (H_2O, HNO_3)	Pt	*p*-Nitrobenzoic acid, oxalic acid	766
Tyrosine (H_2O, H_2SO_4)	PbO_2	*p*-Hydroxyphenylacetic acid, benzoquinone, hydroquinone, HOAc, CO_2, NH_3	759, 761
Histidine (H_2O, H_2SO_4)	PbO_2	Urea (11.1), malonic acid (3), NH_3, polymeric substance	759, 761
2-Pyrrolidinecarboxylic acid (H_2O, H_2SO_4)	PbO_2	Succinimide, pyrrolidine	756
Imidazolylpropionic acid (H_2O, H_2SO_4)	PbO_2	Succinic acid (30.4), succinic acid semialdehyde, urea (1.3), NH_3	760
	Aromatic Amines		
Aniline hydrochloride[d]	C	Induline, azophenine, aniline black	749
Aniline			
(a) (H_2O, H_2SO_4), cpe 0.8 V *vs.* sce	Pt	*p*-Aminodiphenylamine, emeraldine, nigraniline, other polymers	129, 130, 319, 423, 480, 563, 712, 860
(b) (Concd H_2SO_4)	Pt	*p*-Aminophenol, benzoquinone	61, 172, 199, 810
(c) (H_2O, HBr)	. . .	2,4,6-Tribromoaniline	312
(d) (H_2O, HCl)	C	Aniline black, tetrachlorobenzoquinone, trichlorobenzoquinone, trichloroaniline	174, 186, 312
o-Toluidine			
(a) . . .	. . .	Violet dye	320
(b) (H_2O, C_2H_5OH, HCl, NH_4SCN)	C	*p*-Thiocyano-*o*-toluidine (75)	348, 539
m-Toluidine (H_2O, C_2H_5OH, HCl, NH_4SCN)	C	3-Methyl-4-thiocyanoaniline (62)	539
p-Toluidine			
(a) (H_2O, C_2H_5OH, KOH)	Fe	*p,p'*-Azotoluene, 5-amino-2-methyl-*p*-quinone-bis-*p*-tolylimide	102, 320
(b) (H_2O, C_2H_5OH, HCl, NH_4SCN)	C	2-Amino-6-methylbenzothiazole	540
p-Nitroaniline (CH_3CN, C_5H_5N, $NaClO_4$)	Pt	4,4'-Dinitroazobenzene (39.2)	820
p-Chloroaniline			
(a) (CH_3CN, C_5H_5N, $NaClO_4$)	Pt	4,4'-Dichloroazobenzene (24.3), tetra-*p*-chloroazophenine (7.8)	820
(b) (CH_3CN, $LiClO_4$)	Pt	Tar	820
2,4-Dichloroaniline (CH_3CN, C_5H_5N, $NaClO_4$)	Pt	2,2',4,4'-Tetrachloroazobenzene (30.0)	820
Aniline + *p*-chloroaniline (CH_3CN, C_5H_5N, $NaClO_4$)	Pt	Azophenine (7.0), azobenzene (8), *p*-chloroazobenzene (83)	820
p-Chloroaniline + *p*-nitro- or 2,4-dinitroaniline (CH_3CN, C_5H_5N, $NaClO_4$), cpe	Pt	4,4'-Dichloroazobenzene	820
p-Phenylenediamine (CH_3CN, $NaClO_4$), cpe 0.55 V *vs.* sce	Pt	Cation radical[g]	538
Aniline + *o*-toluidine + *p*-toluidine (H_2SO_4)	Pt	Rosaniline	813
p-Anisidine			
(a) (CH_3CN, C_5H_5N, $LiClO_4$)	Pt	4,4'-Dimethoxyazobenzene (5.2), tetra-*p*-methoxyazophenine (8.6)	820
(b) (H_2O, C_2H_5OH, HCl, NH_4SCN)	C	2-Amino-6-methoxybenzothiazole (57)	540
p-Phenetidine (H_2O, C_2H_5OH, HCl, NH_4SCN)	C	2-Amino-6-ethoxybenzothiazole (60)	540
2,4-Dimethylaniline			
(a) (H_2O, C_2H_5OH, KOH)	Fe	Azo-*m*-xylene	102
(b) (H_2O, H_2SO_4)	Pt, PbO_2	2,4-Dimethyl-4-hydroxy-2,5-cyclohexadienone imine (50), 2,4-dimethyl-4-hydroxy-2,5-cyclohexadienone (20–30), 3-hydroxy-2,6-dimethyl-*p*-benzoquinone, 2,5-dimethylhydroquinone	86, 235
(c) (Concd H_2SO_4)	Pt	2,5-Dimethyl-4-hydroxyaniline	235
2,4,6-Tri-*t*-butylaniline (CH_3CN, $LiClO_4$, MgO), cpe 0.80 V *vs.* Ag, Ag^+ (0.01 *M*)	Pt	3,5-Di-*t*-butyl-4-imino-2,5-cyclohexadienone[k]	93
Anthranilic acid (H_2O, CH_3OH, HCl, NaSCN)	C	2-Amino-5-thiocyanobenzoic acid (60)	348
Methyl *p*-aminobenzoate (H_2O, C_2H_5OH, HCl, NH_4SCN)	C	2-Amino-6-carbomethoxybenzothiazole	540
Ethyl *p*-aminobenzoate (H_2O, C_2H_5OH, HCl, NH_4SCN)	C	2-Amino-6-carboethoxybenzothiazole (90)	540
p-Aminodiphenylmethane (H_2O, H_2SO_4), cpe	Pt	Emeraldine	563
4-Amino-4'-methoxydiphenylamine (H_2O, varying pH)	Pt	N-(*p*-Anisyl)-*p*-benzoquinone diimine	31, 187

TABLE X (*Continued*)

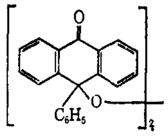
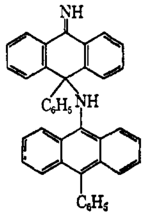
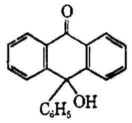
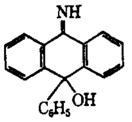
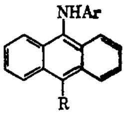
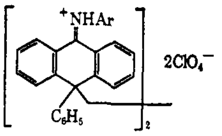
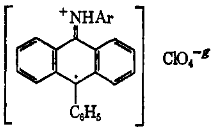
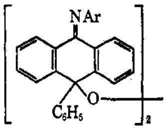
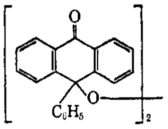
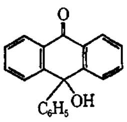
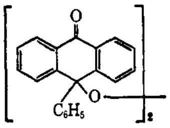
Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
α-Naphthylamine			
(a) (H_2O, acetone, H_2SO_4, $K_2Cr_2O_7$)	PbO_2	1,4-Naphthoquinone	605
(b) (H_2O, CH_3OH, H_2SO_4, $Ca(SCN)_2$)	C	1-Amino-4-thiocyanonaphthalene (55)	348
5,6,7,8-Tetrahydronaphthylamine (H_2O, acetone, H_2SO_4, $KClO_3$)	PbO_2	5,6,7,8-Tetrahydro-1,4-naphthoquinone	605
9-Amino-10-phenylanthracene			
(a) (CH_3CN, $LiClO_4$, N_2) cpe 0.200 V *vs.* Ag, Ag^+ (0.01 *M*)	Pt	9-Amino-10-phenylanthracene cation radical[g]	89, 90
(b) (CH_3CN, $LiClO_4$, O_2), cpe 0.200 V *vs.* Ag, Ag^+ (0.01 *M*)	Pt	 (good yield)	89, 90
(c) (CH_3CN, $LiClO_4$, N_2; diphenylguanidine), cpe <0.170 V *vs.* Ag, Ag^+ (0.01 *M*)	Pt	 (100)	89, 90
(d) (CH_3CN, $LiClO_4$), cpe >0.750 V *vs.* Ag, Ag^+ (0.01 *M*)	Pt	 (excellent yield)	89, 90
(e) (CH_3CN, $LiClO_4$, MgO), cpe 0.750 V *vs.* Ag, Ag^+ (0.01 *M*)	Pt	 (90)	89, 90
			
(a)[l] (CH_3CN, $LiClO_4$), R = H; Ar = C_6H_5, *p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, *p*-$(CH_3)_2C_6H_4$, *p*-$CH_3O_2CC_6H_4$, *p*-$NO_2C_6H_4$, cpe 0.1 V *vs.* Ag, Ag^+ (0.01 *M*) for Ar = *p*-$(CH_3)_2NC_6H_4$	Pt		54, 90, 653
(b)[l] (i) (CH_3CN, $LiClO_4$, N_2), R = C_6H_5; Ar = *p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, *m*-$CH_3OC_6H_4$, *p*-$(CH_3)_2NC_6H_4$, *p*-$C(CN)C(CN)_2C_6H_4$, cpe 0.450 V *vs.* Ag, Ag^+ (0.01 *M*) for Ar = *p*-$CH_3OC_6H_4$	Pt		54, 90, 653
(ii) (CH_3CN, $LiClO_4$, O_2), cpe 0.450 V *vs.* Ag, Ag^+ (0.01 *M*) for Ar = *p*-$CH_3OC_6H_4$, R = C_6H_5	Pt	 (70) 	54, 90, 653
(iii) (CH_3CN, $LiClO_4$), cpe 0.900 V *vs.* Ag, Ag^+ (0.01 *M*) for Ar = *p*-$CH_3OC_6H_4$, R = C_6H_5	Pt	 (good yield) 	54, 90, 653

TABLE X (*Continued*)

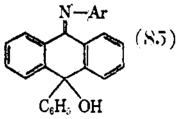
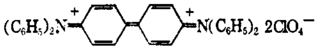
Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
(iv) (CH_3CN, $LiClO_4$, MgO), cpe 0.500 V *vs.* Ag, Ag^+ (0.01 *M*) for Ar = *p*-$CH_3OC_6H_4$, R = C_6H_5	Pt	 (85)	54, 90, 653
N-Methylaniline			
(a) (H_2O, pH 2.4), cpe	Pt, C paste		297
(b) (H_2O, C_2H_5OH, HCl, NH_4SCN)	C	*p*-Thiocyano-N-methylaniline (41)	787
(c) (H_2O, C_2H_5OH, KSeCN)	C	*p*-Selenocyano-N-methylaniline (10)	541
(d) (C_5H_5N, AgCN)	Pt	Oxamidine derivative	699
(e) (Liq NH_3, salicylic acid)	Pt	1,2-Dimethyl-1,2-diphenylhydrazine (4), polymer	317
N-Ethylaniline			
(a) (H_2O, C_2H_5OH, HCl, NH_4SCN)	C	*p*-Thiocyano-N-ethylaniline (60)	539
(b) (H_2O, C_2H_5OH, KSeCN)	C	*p*-Selenocyano-N-ethylaniline (10)	541
N-Propylaniline (H_2O, C_2H_5OH, HCl, NH_4SCN)	C	*p*-Thiocyano-N-propylaniline (44)	787
N-Butylaniline (H_2O, C_2H_5OH, HCl, NH_4SCN)	C	*p*-Thiocyano-N-butylaniline (68)	787
N-Benzylaniline (H_2O, C_2H_5OH, HCl, NH_4SCN)	C	*p*-Thiocyano-N-benzylaniline (84)	787
p-Nitrobenzylaniline (CH_3CN, C_5H_5N, $NaClO_4$)	Pt	1,2-Diphenyl-1,2-bis(*p*-nitrobenzyl)hydrazine (0.3 g/1.0 gsm)	821
N-Ethyl-*m*-toluidine (H_2O, C_2H_5OH, HCl, NH_4SCN)	C	3-Methyl-4-thiocyano-N-ethyltoluidine (60)	787
2-Methylaminobenzoic acid (H_2O, C_2H_5OH, HCl, NH_4SCN)	C	2-Methylamino-4-thiocyanobenzoic acid (63)	787
Diphenylamine (CH_3CN, $NaClO_4$), cpe 0.640 V *vs.* sce	Pt	Dibenzylbenzidine, diphenylbenzidine violet[i]	160
Di-4-tolylamine (CH_3CN, $NaClO_4$), cpe 0.8 V *vs.* sce	Pt	Phenazine derivatives	160
Diphenylbenzidine (CH_3CN, $NaClO_4$), cpe	Pt	Diphenylbenzidine violet	160
1,2,3,4-Tetrahydroquinoline (H_2O, H_2SO_4)	PbO_2	Gentisic acid, propionic acid, maleic acid, oxalic acid, HCO_2H, NH_3, CO_2, CO	867
N,N-Dimethylaniline			
(a) (H_2O, H_2SO_4)	Pt, PbO_2	N,N-Dimethylaniline N-oxide; N,N,N′,N′-tetramethylbenzidine (42), N,N,N'-trimethylphenyl-*p*-phenylenediamine, N,N,N',N'-tetramethyl-4,4'-diaminodiphenylmethane	244, 497
(b)[g] (1) (H_2O, pH 2–3),[h] cpe 0.8 V *vs.* sce (2) (HOAc, $NaClO_4$), cpe 0.8 V *vs.* Ag|AgCl (3) (CH_3CN, $NaClO_4$), cpe 0.9 V *vs.* sce	Pt, C		156, 160, 295, 300, 555
(c) (CH_3OH, KOH), cpe 1.20 V *vs.* sce	Pt	N-Methoxymethyl-N-methylaniline (68), N,N-bis-(methoxymethyl)aniline (3)	831, 832
(d) (CH_3OH, NH_4NO_3), cpe 1.20 V *vs.* sce	Pt	N,N,N',N'-Tetramethylbenzidine mononitrate salt (0.15 mole/faraday)	832
(e) (H_2O, C_2H_5OH, HCl, NH_4SCN)	C	*p*-Thiocyano-N,N-dimethylaniline (92)	248, 348
(f) (H_2O, C_2H_5OH, HCl, KSeCN)	C	*p*-Selenocyano-N,N-dimethylaniline (20)	541
N,N-Diethylaniline			
(a) (H_2O, H_2SO_4)	PbO_2	N,N,N',N'-Tetraethylbenzidine	244
(b) (H_2O, C_2H_5OH, HCl, NH_4SCN)	C	*p*-Thiocyano-N,N-diethylaniline (69)	248
(c) (H_2O, C_2H_5OH, HCl, KSeCN)	C	*p*-Selenocyano-N,N-diethylaniline (20)	541
N,N-Dimethyl-*p*-toluidine			
(a) (H_2O, pH 2–6)	C paste, Pt	*o,o'*-Dimethyl-N,N′-tetramethylbenzidine (nil), *p*-dimethylaminobenzoic acid, *p*-dimethylaminobenzaldehyde	297
(b) (H_2O, C_2H_5OH, HCl, NH_4SCN)	C	*o*-Thiocyano-N,N-dimethyl-*p*-toluidine (21)	248
N,N-Dimethyl-2,4-dimethylaniline (H_2O, H_2SO_4)	Pt, PbO_2	2,4-Dimethyl-4-hydroxy-2,5-cyclohexadienone (36), 2,4-dimethyl-4-hydroxy-2,5-cyclohexadienone methylimine	235
N-Methyl-N-ethylaniline (CH_3CN, $(C_2H_5)_4NCN$), cpe	Pt	N-α-Cyanoethyl-N-methylaniline, N-cyanomethyl-N-ethylaniline (ratio 1:2)	14
N-Methoxymethyl-N-methylaniline (CH_3OH, KOH)	Pt	N,N-Bis(methoxymethyl)aniline (33)	831
Triphenylamine (CH_3CN, $NaClO_4$), cpe 0.690 V *vs.* sce; also cpe 1.0 V *vs.* sce	Pt	N,N,N',N'-Tetraphenylbenzidine and cation radical, 	160, 583, 708
Tri-*p*-tolylamine (CH_3CN, $(C_2H_5)_4NCN$), cpe	Pt	Cation radical	708
Tri-*p*-anisylamine (CH_3CN, $(C_2H_5)_4NCN$), cpe	Pt	Cation radical	708
Tri-*p*-chlorophenylamine (CH_3CN, $NaClO_4$), cpe	Pt	Cation radical	708
Tri-*p*-bromophenylamine (CH_3CN, $NaClO_4$), cpe	Pt	Cation radical	708
N,N-Di-*p*-methoxyphenylaniline (CH_3CN, $NaClO_4$), cpe	Pt	Cation radical	708
N,N-Diphenyl-*p*-anisylamine (CH_3CN, $NaClO_4$), cpe	Pt	Cation radical	708
N-Methyl-N-*p*-methoxyphenylaniline (CH_3CN, $NaClO_4$), cpe	Pt	Cation radical	708

TABLE X (*Continued*)

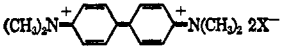
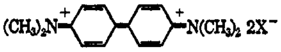
Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
N,N-Di-*p*-methoxyphenyl-N-methylaniline (CH_3CN, $NaClO_4$), cpe	Pt	Cation radical[i]	708
N,N-Dimethyl-*p*-anisylamine (CH_3CN, $NaClO_4$), cpe	Pt	Cation radical[i]	708
N,N-Di-*p*-methylphenyl-N-methylaniline (CH_3CN, $NaClO_4$), cpe	Pt	Cation radical[i]	708
N,N,N′,N′-Tetramethylbenzidine (H_2O, acetone, pH 2.9), cpe	Pt	Cation radical	290
Triphenylmethane Dyes			
Crystal violet Malachite green *p,p*′-Methylenebis(N,N-dimethylaniline) (H_2O, acid)	C, Pt	N,N,N′,N′-Tetramethylbenzidine,  central carbon moiety	296, 298
Ethyl violet Brilliant green (H_2O, acid)	C, Pt	N,N,N′,N′-Tetraethylbenzidine,  central carbon moiety	296, 298
N,N,N′,N′-Tetramethyl-4,4′-diaminodiphenylmethane (H_2O, H_2SO_4)	PbO_2	N,N,N′,N′-Tetramethyl-4,4′-diaminobenzhydrol	190
N,N,N′,N′-Tetraethyl-4,4′-diaminodiphenylmethane (HOAc)	Pt	N,N,N′,N′-Tetraethyl-4,4′-diaminobenzhydrol	190
4,4′-Bisdimethylamino-2,2′-dimethyldiphenylmethane (H_2O, Na_2SO_4)	PbO_2	4,4′-Bisdimethylamino-2,2′-dimethylbenzhydrol (quant)	661
Leucomalachite green (H_2O, H_2SO_4, UO_2SO_4)	PbO_2, Ni, Pt, C	Malachite green (57)	506, 833
Leucobrilliant green (H_2O, Na_2SO_4, Na_2CO_3)	C–Pt,[l] Pt	Brilliant green (89.3)	833
Leucoguinea green (H_2O, Na_2CO_3)	Pt	Guinea green (59.8)	833
Leucocrystal violet (H_2O, pH 1.1), cpe 1.00 V *vs.* sce	Pt	Crystal violet (30–40), N,N,N′,N′-tetramethylbenzidine,  *p*-dimethylaminobenzoic acid	658
Heterocyclic Amines			
N-Methylpyrrole (CH_3OH, KOH)	Pt	N-Methyl-2,2,5,5-tetramethoxy-3-pyrroline (57)	830
Histamine (H_2O, H_2SO_4)	PbO_2	Urea (9), *β*-alanine (8.5), CO_2, NH_3	768
3,5-Dimethylpyrazole (H_2O, Na_2SO_4)	PbO_2	Pyrazole-3-carboxylic acid	216
1-Phenyl-3-methylpyrazole			
(a) (H_2O, K_2CO_3)	Pt	Pyrazole-3-carboxylic acid	216
(b) (H_2O, H_2SO_4)	PbO_2	Hydroquinone, benzoquinone, oxalic acid	216
Pyridine			
(a) (H_2O, H_2SO_4)	Pt, PbO_2	2-Pyridylpyridinium sulfate, glutacondialdehyde, CO_2, CO, HNO_3, HCO_2H, NH_3, CH_2O	37, 38, 864
(b) ($LiClO_4$ or $(C_2H_5)_4NClO_4$), cpe 1.6 V *vs.* Ag, Ag^+ (1.0 *M*)	C	2-Pyridylpyridinium perchlorate	790
(c) (CH_3CN, $(C_2H_5)_4NCN$), cpe	Pt	2-Cyanopyridine (15)	14
2-Vinylpyridine	. . .	2-Pyridylethylene glycol (6), 2-pyridinecarboxaldehyde (3)	201
2-Aminopyridine (H_2O, CH_3OH, KI)	. . .	2-Amino-5-iodopyridine	147
2-Picoline (H_2O, H_2SO_4)	PbO_2	Picolinic acid (20–30), HCO_2H, HOAc, picolylalkine, NH_3, HNO_3, CO_2, CO	861
Picolinic acid (H_2O, H_2SO_4)	PbO_2	HCO_2H, NH_3, HCHO	861
3-Picoline (H_2O, H_2SO_4)	PbO_2	Nicotinic acid (65)	425, 426, 454
4-Picoline (H_2O, H_2SO_4)	Pt, PbO_2	Isonicotinic acid (42.5), 4-picolinealdehyde (16.8)	201, 383, 579
4-Ethylpyridine (H_2O, HNO_3)	Pt	Isonicotinic acid (75)	383, 579
2,4-Lutidine (H_2O, H_2SO_4)	PbO_2	Lutidinic acid (22)	427
2-Methyl-5-ethylpyridine (H_2O, H_2SO_4)	PbO_2	Isocinchomeronic acid	64
2,6-Dimethoxypyridine (CH_3OH, KOH)	Pt	2,3,3,6,6-Pentamethoxy-1,4-azacyclohexadiene (26), 2,3,5,6-tetramethoxypyridine, 2,3,6-trimethoxypyridine	830
Nicotine (H_2O, $KMnO_4$)	Ni, Fe	Nicotinic acid (77–82)	504
Quinoline			
(a) (H_2O, H_2SO_4)	Pt, PbO_2	Quinolinic acid (77)	119, 123, 425, 454, 788
(b) (H_2O, H_2SO_4)	PbO_2	Quinolinic acid, *o*-carboxycinnamic acid, HCO_2H, NH_3, HNO_3, CO_2, CO	866
3-Fluoroquinoline (H_2O, H_2SO_4)	Pt	5-Fluoroquinolinic acid (26)	119
3-Chloroquinoline (H_2O, H_2SO_4)	Pt	5-Chloroquinolinic acid (54)	119
3-Bromoquinoline (H_2O, H_2SO_4)	PbO_2	5-Bromoquinolinic acid (73)	119

TABLE X (*Continued*)

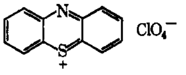
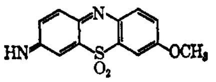
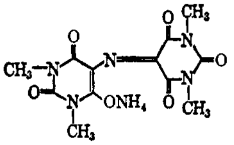
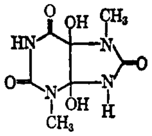
Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
3-Iodoquinoline (H_2O, H_2SO_4)	Pt	5-Hydroxyquinolinic acid hemihydrate (10)	119
3-Aminoquinoline, 2-chloroquinoline, 4-chloroquinoline, or 2-phenylquinoline (H_2O, H_2SO_4)	Pt, PbO_2	No quinolinic acid, polymeric material isolated	119
Quinoxaline (H_2O, NaOH, $KMnO_4$)	Cu	2,3-Pyrazinecarboxylic acid (91.7)	417
Dihydroquinacridone (H_2O, CH_3OH, NaOH)	Ni	Quinacridone (quant)	9
9,10-Dihydrophenazine (CH_3CN, $(n\text{-}C_3H_7)_4NClO_4$), cpe	Hg	Cation radical	339
5,10-Dihydro-5,10-dimethylphenazine (H_2O, acetone, pH 1.5),[o] cpe 1.1 V *vs.* sce	Pt	5,10-Dihydro-5-methylphenazine	584
Phenothiazine			
(a) (CH_3CN, $LiClO_4$), cpe 0.50 V *vs.* Ag, Ag^+ (0.01 *M*)	Pt	Phenothiazine cation radical[p] (quant)	48, 49, 50–53
(b) (CH_3CN, $LiClO_4$), cpe 0.90 V *vs.* Ag, Ag^+ (0.01 *M*)	Pt		48, 49, 50, 53
(c) (H_2O, C_2H_5OH, H_2SO_4), cpe −0.25 V *vs.* Hg, $HgSO_4$ (satd) in 10 *N* H_2SO_4 and 30% C_2H_5OH	Hg	Phenothiazine cation radical	414
10-[3-(4-β-Hydroxyethyl-1-piperazinyl)propyl]-2-chlorophenothiazine (H_2O, H_2SO_4), cpe 0.8 V *vs.* normal calomel electrode	Au	Corresponding sulfoxide (0.855 g/gsm)	397
Chlorpromazine (H_2O, H_2SO_4),[m] cpe 0.70 V *vs.* sce	Pt	Chlorpromazine 5-oxide (quant)	544, 545, 547
Promethazine Promazine Triflupromazine Prochlorperazine Thioridazine (H_2O, H_2SO_4)			
(a) cpe 0.55 to 0.70 V *vs.* sce	Pt	Cation radical[n] (quant)	547
(b) cpe 0.75 to 1.05 V *vs.* sce	Pt	Corresponding sulfoxide	547
10-Methylphenothiazine (CH_3CN, H_2O, $HClO_4$, $LiClO_4$), cpe 0.6 V *vs.* Ag, Ag^+ (0.01 *M*)	Pt	Cation radical	51
2,7,10-Trimethylphenothiazine (CH_3CN, $LiClO_4$), cpe	Pt	Corresponding dication[q]	51
2-Amino-7-methoxyphenazine 9-dioxide (aqueous solution), cpe	Hg		187
N-Methyl-1,3,4,7-tetraphenylisoindole (DMF, $(n\text{-}C_4H_9)_4NClO_4$), cpe	Pt	Cation radical[p]	893
N-Methyl-1,3-di-*p*-anisyl-4,7-diphenylisoindole (DMF, $(n\text{-}C_4H_9)_4NClO_4$), cpe	Pt	Cation radical[p]	893
Caffeine			
(a) (H_2O, HOAc)	Pt	 (10.9)	223
(b) (H_2O, H_2SO_4)	PbO_2	Dimethylmesoxalylurea, CH_3NH_2, HCO_2H, NH_3	223, 637
Desoxycaffeine (H_2O, Na_2SO_4)	PbO_2	Dimethylparabanic acid (11.6)	223
Theobromine (H_2O, H_2SO_4)	PbO_2	 monomethylmesoxalylurea (60), monomethylparabanic acid, urea, CH_3NH_2, HCO_2H, NH_3	223, 671
Desoxytheobromine (H_2O, H_2SO_4)	PbO_2	Monomethylparabanic acid (51.6), CH_3NH_2, NH_3, CO_2	223
Brucine (H_2O, H_2SO_4)	PbO_2	Dehydrobisapomethylbrucine	257
Persantine			
(a) (CH_3CN, $LiClO_4$), cpe 0.30 V *vs.* Ag, Ag^+ (0.01 *M*)	Pt	Persantine cation radical	464
(b) (CH_3CN, $LiClO_4$), cpe 0.60 V *vs.* Ag, Ag^+ (0.01 *M*)	Pt	Red solution	464
		Quaternary Ammonium Salts	
N-Methylpyridinium sulfate (H_2O, NaOH, $K_3Fe(CN)_6$)	Fe	N-Methyl-2-pyridone (95)	279, 280, 590
N-Methylquinolinium sulfate (H_2O, NaOH, $K_3Fe(CN)_6$)	Fe	N-Methyl-2-quinolone (quant)	280
8-Methyl-N-methylquinolinium sulfate (H_2O, NaOH, $K_3Fe(CN)_6$)	Fe	8-Methyl-N-methyl-2-quinolone (90)	590

Table X (*Continued*)

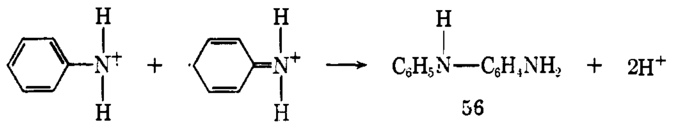
Compound (solvent, electrolyte)	Anode	Products(s) (% yield)	Ref
6-Methyl-N-methylquinolinium sulfate (H_2O, NaOH, $K_3Fe(CN)_6$)	Fe	6-Methyl-N-methyl-2-quinolone (75)	590
6-Methoxy-N-methylquinolinium sulfate (H_2O, NaOH, $K_3Fe(CN)_6$)	Fe	6-Methoxy-N-methyl-2-quinolone (good)	279
8-Methoxy-N-methylquinolinium sulfate (H_2O, NaOH, $K_3Fe(CN)_6$)	Fe	8-Methoxy-N-methyl-2-quinolone	279
N-Methylnaphthoquinolinium sulfate (H_2O, NaOH, $K_3Fe(CN)_6$)	Fe	N-Methylnaphthoquinolone (quant)	590
N-Methylacridinium sulfate (H_2O, NaOH, $K_3Fe(CN)_6$)	Fe	N-Methylacridone	590
Tetraethylammonium cyanide (CH_3CN), cpe 2.0 V *vs.* sce	Pt	α-Diethylaminopropionitrile (39), C_2H_4	14
Quaternary ammonium halide (H_2O)	C, Pt	Quaternary ammonium hydroxide	451, 746
Quaternary ammonium iodide (H_2O, chloride[s] or bromide[s])	Pt	Quaternary ammonium chloride or bromide	451

[a] At least 50% of the amine was recovered in the unreactive protonated form. [b] Amines (CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$) are produced by subsequent condensation of HCHO and NH_3. [c] Volatile oxidation products removed from electrolysis cell as formed. [d] Molten salt with added aniline at 160°. [e] Electrochemical kinetic study. [f] Dye pressed with carbon on platinum. [g] Observed by esr. [h] Evidence was found for a small amount of *ortho–para* coupled product. [i] Major product. [j] The cation radical is stable even in 50% acetone–water buffers from pH 2 to 6. [k] 2,4,6-Tri-*t*-butylaniline cation radical observed by cyclic voltammetry and esr. [l] Corresponding cation radicals observed by esr. [m] The stable solid free radical of chlorpromazine has been prepared (546). [n] Cation radical is stable in 12 *N* H_2SO_4. [o] The cation radical is stable in CH_3CN, DMSO, DMF, CH_3OH, and acetone–buffer mixtures. [p] Observed by electrochemiluminescence, cyclic voltammetry, and esr. [q] Reacts with water to form the sulfoxide. [r] At a Hg anode, a mercurial is formed. [s] In cathode compartment. [t] Isolated as pyrazine derivative.

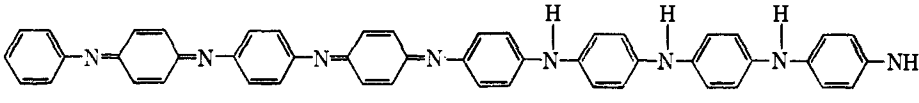
tail condensation mechanism depicted by Eq 39–41 for the initial steps.

$$C_6H_5NH_3^+ \rightleftharpoons C_6H_5NH_2 + H^+ \qquad \text{(Eq 39)}$$

$$2C_6H_5NH_2 \longrightarrow 2C_6H_5NH_2^{\cdot+} + 2e \qquad \text{(Eq 40)}$$



(Eq 41)

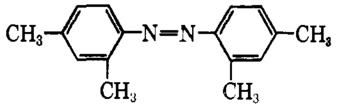


57

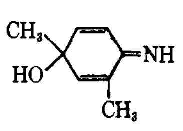
Anodic thiocyanation of aromatic amines occurs with introduction of the thiocyano group *para* to the amino function. When the *para* position is blocked, substitution may occur at a free *ortho* position. In the case of *para*-substituted primary aromatic amines, aminobenzothiazole derivatives are formed in a subsequent condensation step. These compounds probably result from reaction of free thiocyanogen released in the electrolysis of thiocyanide salts, since it is known that in homogeneous solution thiocyanogen readily reacts with aromatic amines and the products are identical (404, 405). Several examples of selenocyanation have been reported.

Depending on conditions aromatic amines may be oxidized to a variety of products. An Fe anode in basic solution seems to favor formation of azo derivatives. Thus 2,4-dimethylaniline affords azo-*m*-xylene (**58**) (102). At Pt or PbO_2 anodes in dilute H_2SO_4, the cyclohexadienone imine **59**, the hydrolysis product **60**, and a small quantity of 3-hydroxy-2,6-dimethyl-*p*-benzoquinone (**61**) are formed. At elevated temperatures 2,5-dimethylhydroquinone (**62**) results from rearrangement of **60**. In concentrated H_2SO_4 solution, 2,5-dimethyl-4-hydroxyaniline (**63**) is formed from **59**. Many of the above products have been obtained by chemical oxidation of 2,4-dimethylaniline (235): **61**, ferric chloride in dilute H_2SO_4; **59** and **60**, permonosulfuric acid; **58**, potassium ferricyanide or potassium permanganate in neutral and alkaline solution. Wawzonek and McIntyre have studied the oxidation of anilines at a rotating platinum electrode in CH_3CN solution (820). In the presence of pyridine, the reaction involves a two-electron change, and azobenzenes are formed. Good yields of mixed azobenzenes (*i.e.*, *p*-chloroazobenzene from aniline and *p*-chloroaniline) may be obtained under conditions of constant voltage, while cpe affords only the azobenzene of the most easily oxidized aniline. In the absence of pyridine the behavior of anilines is more complex.

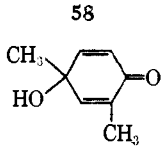
Cpe of 2,4,6-tri-*t*-butylaniline (**64**) in CH_3CN results in loss of the *p*-*t*-butyl group to give 3,5-di-*t*-butyl-4-imino-2,5-cyclohexadienone (**69**) (93). Cyclic



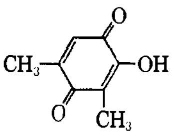
58



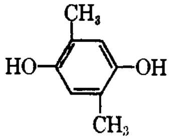
59



60



61



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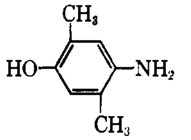
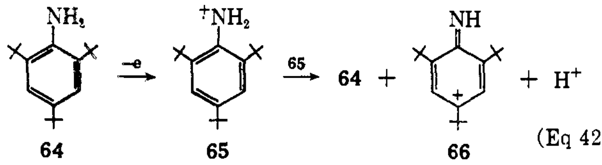
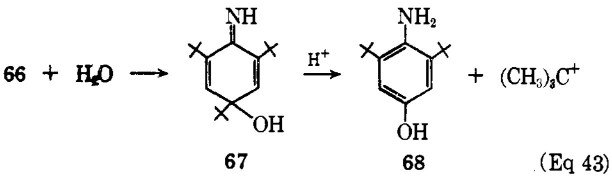


63

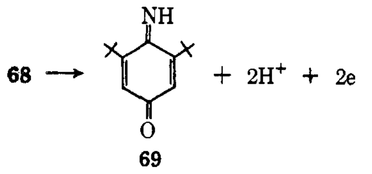
voltammetry and esr studies have demonstrated the existence of radical **65**, and a coulometric analysis has established that four electrons per molecule are transferred in total. The reaction requires traces of water, since prolonged drying of the solvent gives a low yield of **69**. The reaction mechanism has been described as proceeding by disproportionation of **65** to **64** and the cation **66**. The latter then reacts with water forming an unstable iminoquinol **67** which undergoes spontaneous decomposition to the aminophenol **68**, followed by further oxidation to product **69** (Eq 42–44).



(Eq 42)

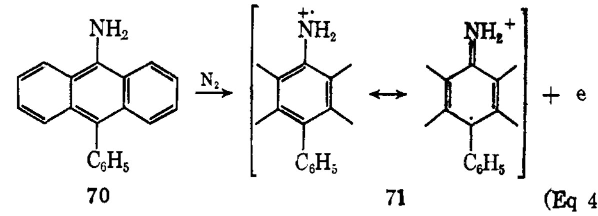


(Eq 43)

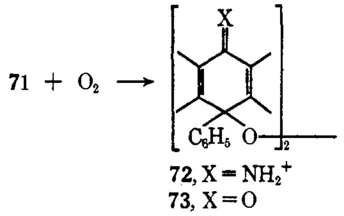


(Eq 44)

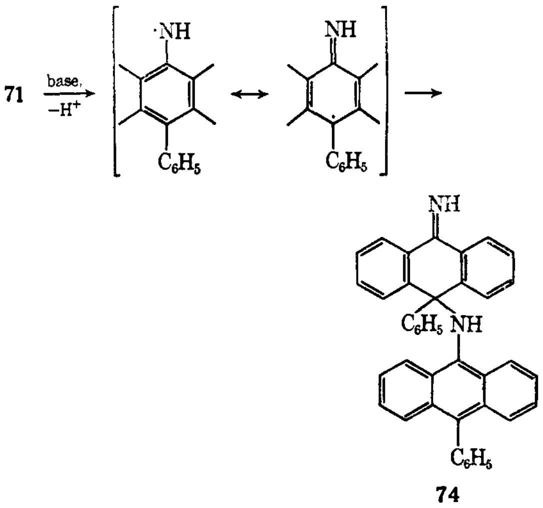
Substituted 9-aminoanthracene derivatives have exhibited a variety of interesting reactions on cpe in CH_3CN (54). The 10-phenyl derivative **70** shows two anodic waves in its current–voltage curve corresponding to two single-electron transfers. Cpe under nitrogen at a potential between the two steps provides the corresponding cation radical **71** (Eq 45). In an atmosphere of oxygen, however, the peroxide **72** is formed and is isolatable as the ketonic peroxide **73** (Eq 46). A solution of **71** is converted to the *head-to-tail* dimer **74** in presence of base (diphenylguanidine). Cpe at a potential more anodic than the second wave produces the dication which eventually reacts with traces of water to give the imino alcohol **75**. On prolonged electrolysis, the ketone **76** may be obtained. N-Substituted 9-aminoanthracenes afford an additional product, the dimer **77**, resulting from *head-to-tail* dimerization of the intermediate cation radicals. Analogous oxidation products have been obtained with potassium permanganate or potassium ferricyanide in alkaline solution (87, 666).



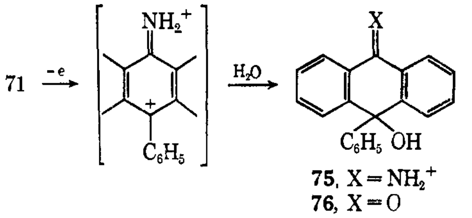
(Eq 45)



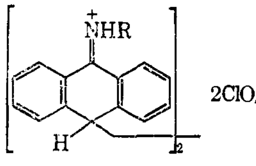
(Eq 46)



(Eq 47)



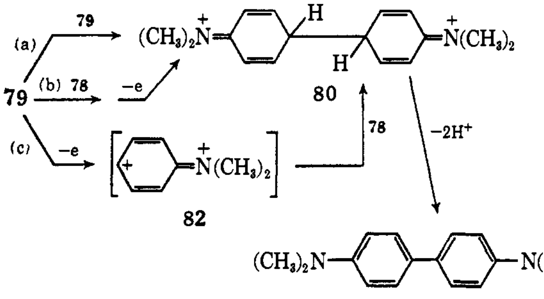
(Eq 48)



77

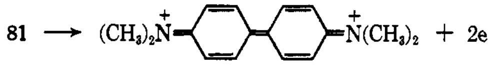
Depending on reaction conditions, the electrolysis products of N,N-dimethylaniline (**78**) may result from oxidation of the aromatic ring or the N-methyl group. In aqueous acid (295, 300, 555), anhydrous acetic acid (156), or CH_3CN (160) at Pt or carbon paste anodes the oxidized form of tetramethylbenzidine (**83**) is obtained. Electrochemical kinetic studies have shown that the reaction order for **78** is unity in aqueous acid. No evidence for a cation radical intermediate **79** could be found, and a mechanism involving the dication species **82** was originally proposed (Eq 49, 50c, 51). A later publication (708) has pointed out that the observed electrochemical kinetics are best interpreted by formation of cation radical **79** followed by a fast chemical reaction. The course of the reaction in anhydrous acetic acid illustrated in Eq 49, 50a, and 51 agrees with the experimental results of a reaction order of two for **78** with one electron involved in the rate-controlling step.

$$\underset{\mathbf{78}}{C_6H_5N(CH_3)_2} \longrightarrow \underset{\mathbf{79}}{C_6H_5\overset{+\cdot}{N}(CH_3)_2} + e \qquad \text{(Eq 49)}$$



(Eq 50)

81



(Eq 51)

83

Earlier investigations of oxidation of **78** in dilute H_2SO_4 have shown that tetramethylbenzidine, tetramethyldiaminodiphenylmethane, and trimethylphenyl-*p*-phenylenediamine may be obtained at Pt or PbO_2 anodes. Fichter and Rothenberger proposed a reaction scheme involving condensation of formaldehyde (released by oxidative attack at N-methyl) with **78** or N-methylaniline to account for the last two products (244).

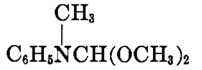
Electrochemical kinetic studies of oxidation of **78** in CH_3OH containing KOH or NH_4NO_3 as electrolytes show the reaction order to be fractional with respect to **78** owing to adsorption (832). One electron is transferred in the rate-controlling step for each of these systems. Surprisingly, the resultant products in each case are totally different. The basic CH_3OH solution affords N-methoxy-N-methylaniline (**84**) and N,N-bis-(methoxymethyl)aniline (**85**) (831). No N-dimethoxymethyl-N-methylaniline (**86**) was observed although **86** was expected as a further oxidation product on the basis of chemical oxidations of **78** (29, 349). The NH_4NO_3–CH_3OH medium provided the mononitrate salt of **81** as a precipitate on the anode. The diversity in products has been explained in terms of mechanisms incorporating the pH of the solution. The function of the basic system is then to assist deprotonation of the adsorbed cation radical formed in the rate-determining step. Loss of a second electron followed by reaction of the resultant cation with solvent would lead to **84**. Further oxidation of **84** is pictured as proceeding *via* the maximally adsorbed configuration of **84** (aromatic ring, nitrogen, and oxygen centers adsorbed) to produce **85**. In the absence of base, the adsorbed cation radical can only undergo a dimer-forming reaction (Eq 50).

$C_6H_5\overset{\overset{\displaystyle CH_3}{|}}{N}CH_2OCH_3$

84

$C_6H_5N(CH_2OCH_3)_2$

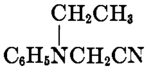
85



$C_6H_5\overset{\overset{\displaystyle CH_3}{|}}{N}CH(OCH_3)_2$

86

The electrochemical cyanation of N-methyl-N-ethylaniline is a novel reaction which is possibly related to the methoxylation of **78** (14). Twice as much N-cyanomethyl-N-ethylaniline (**87**) as N-α-cyanoethyl-N-methylaniline (**88**) is formed.



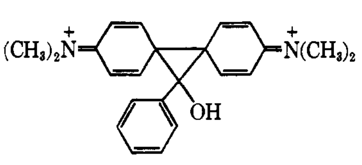
$C_6H_5\overset{\overset{\displaystyle CH_2CH_3}{|}}{N}CH_2CN$

87

$C_6H_5\overset{\overset{\displaystyle CH_3}{|}}{N}CHCNCH_3$

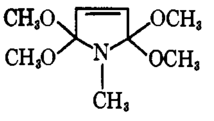
88

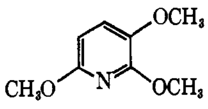
Chemical (336, 406, 428) and electrochemical oxidations (296, 298, 658) of triphenylmethane dyes appear to be analogous processes since in each case the dye is transformed to a benzidine derivative with ejection of a central carbon fragment. Paradoxically the protonated hydrated form of the dye is easier to oxidize than the nonprotonated form, suggesting that not the amino functions, but the central carbon is oxidized. An initial two-electron charge-transfer step has been proposed followed by a series of chemical interactions whereby the benzidine derivative is produced in an intracoupling process of two dimethylanilino groups. A cyclopropane intermediate (**89**) has been suggested (336).



89

The anodic methoxylation of N-methylpyrrole, unlike the methoxylation of furans in which dimethoxylation occurs, results in 1-methyl-2,2,5,5-tetramethoxy-3-pyrroline (**90**) (830). No di- or trimethoxypyrrolines were found although these are reasonable intermediates to **90**. Further methoxylation beyond the dimethoxypyrroline level probably occurs *via* pathways which are analogous to those described for methoxylation of N,N-dimethylaniline. Methoxylation of 2,6-dimethoxypyridine results in products which are similar to those obtained from 1,3-dimethoxybenzene (section III.A.2), giving 2,3,6-trimethoxypyridine (**91**), 2,3,5,6-tetramethoxypyridine (**92**), and 2,3,3,6,6-pentamethoxy-1,4-azacyclohexadiene (**93**).


90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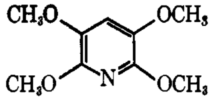
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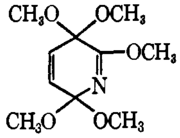
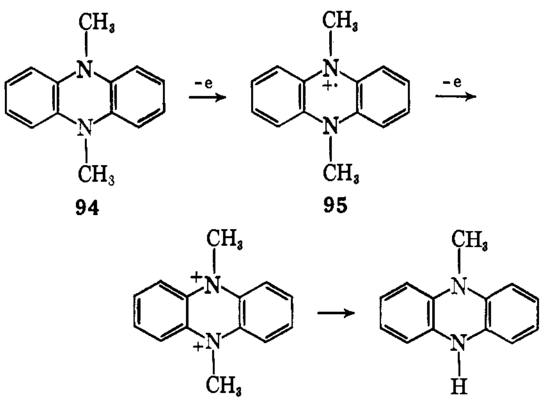
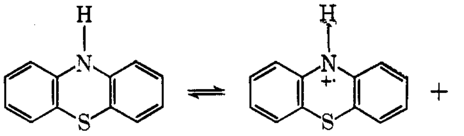

93

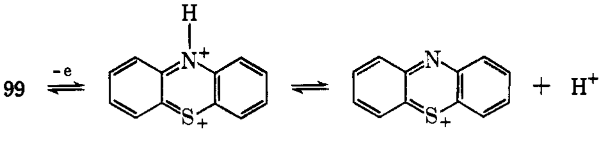
Pyridine itself is oxidized either in aqueous solution or in pyridine as solvent to 2-pyridylpyridinium salts and glutacondialdehyde (hydrolysis product). In CH_3CN containing tetraethylammonium cyanide as electrolyte, substitution occurs at the 2 position to give 2-cyanopyridine (14). In contrast, oxidation of alkyl-substituted heterocycles at a variety of anodes in aqueous acidic or basic solution results in side-chain oxidation to the corresponding heterocyclic carboxylic acid. Quinoline and quinoxaline behave similarly and give excellent yields of quinolinic acid and 2,3-pyrazinecarboxylic acid, respectively.

The heterocycle 5,10-dihydro-5,10-dimethylphenazine (**94**) exhibits two successive reversible one-electron oxidation–reduction steps in CH_3CN. Cpe at a potential between the two waves produces the stable cation radical **95**. At a potential more anodic than the second wave, oxidative demethylation occurs in DMSO, DMF, and aqueous acetone buffers, resulting in the monomethylphenazine **97**. Demethylation also occurs in CH_3CN if strong cation-solvating compounds or nucleophiles such as pyridine N-oxide or chloride ion are present. A nucleophilic attack on the dication **96** has been assumed in which a 5-methylphenazinium-type intermediate is formed and is protonated (584).


94 **95** **96** **97** (Eq 52)

A variety of phenothiazines including the parent compound **98** has been studied using cpe (51, 397, 414, 545, 547). Two oxidation waves are observed for **98** in CH_3CN which correspond to the stable phenothiazine cation radical **99** and the cation **101**. Water reacts with **101** giving a green compound of unknown structure which may be converted to 3-phenothiazone in the presence of base (alumina or diphenylguanidine). Neither acid nor base have any effect on the first oxidation step (Eq 53), but the second electron-transfer process is markedly influenced. This is due to the equilibrium which exists between **100** and **101** (Eq 54) causing the presence of acid to raise the oxidation potential of **98** and base to lower it.


98 **99** (Eq 53)


100 **101** (Eq 54)

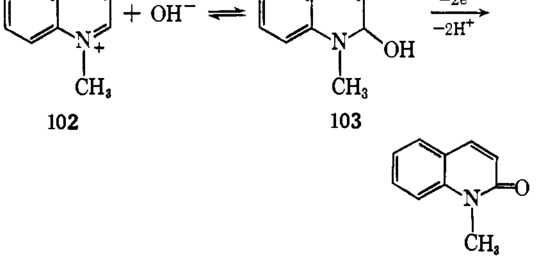
Cpe of N-substituted phenothiazines in aqueous acid provides an excellent method of preparation of the corresponding sulfoxides. Two routes of oxidation are apparent, depending on the concentration of acid. In 12 *N* H_2SO_4 the cation radical ($R\cdot^+$) derived from the phenothiazine (R:) is greatly stabilized, and two discrete oxidation steps may be observed corresponding to formation of the cation radical (Eq 55) and the sulfoxide (S) (Eq 56). In 1 *N* H_2SO_4 a single oxidation wave appears, due to spontaneous disproportionation of the cation radical (Eq 57) (547).

$$R\colon \rightarrow R\cdot^{+} + e \tag{Eq 55}$$

$$R\cdot^{+} + H_2O \xrightarrow[H_2SO_4]{12\,N} S + 2H^{+} + e \tag{Eq 56}$$

$$2R\cdot^{+} + H_2O \xrightarrow[H_2SO_4]{1\,N} R\colon + S + 2H^{+} \tag{Eq 57}$$

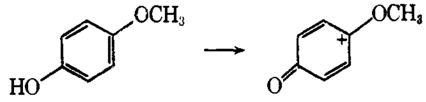
N-Methylquinolones (**104**) are formed on electrolysis of N-methylquinolinium salts (**102**) at an Fe anode in basic solution. The reaction probably involves oxidation of the pseudo-base **103** (resulting from reaction of the quaternary ammonium salt with base) (Eq 58).


102 **103** (Eq 58) **104**

D. OXIDATION OF PHENOLS AND AMINOPHENOLS (TABLE XI)

The course of electrooxidation of phenols is generally similar to that for aromatic primary amines and likewise is highly dependent on the pH of the medium. Thus phenols may be hydroxylated, thiocyanated, and halogenated, and they react to form dimeric products. Hydroxylation of the simpler phenols of comparatively high half-wave potential provides a large number of products.

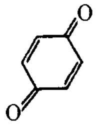
The oxidation of *p*-methoxyphenol (**105**) has been studied at a carbon paste electrode in acid solution (340). With the aid of several diagnostic techniques the mechanism has been established as a two-electron charge transfer to give the dienone **106** followed by rapid hydrolysis to benzoquinone and CH_3OH (Eq 59 and 60). The scheme is in accord with that proposed for oxidation of alkoxyphenols with sodium metaperiodate (5, 6).



$+ H^+ + 2e$

105 106 (Eq 59)

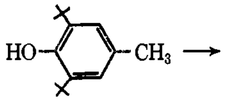
106 + H_2O →



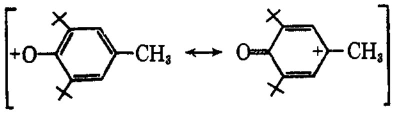
$+ CH_3OH + H^+$ (Eq 60)

107

The formation of cyclohexadienones from suitably substituted phenols appears to be analogous to alkoxylation of aromatic ethers (section III.A.2). Oxidation of the *p*-cresol **108** in CH_3CN containing CH_3OH added gradually during the course of reaction has been examined by Vermillion and Pearl (808) and found to give a mixture of the dienone **110** (65%) and the benzoquinone **111** (10%). A two-electron transfer of **108** to afford the phenoxonium ion **109** (Eq 61) followed by reaction with CH_3OH to form **110** has been suggested. The benzoquinone **111** is believed to result from stepwise oxidation of the *p*-methyl group of **108** *via* a free-radical mechanism, with decarboxylation of the intermediate acid.

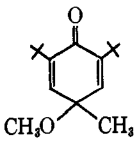


108

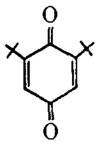


$+ 2H^+ + 2e$ (Eq 61)

109

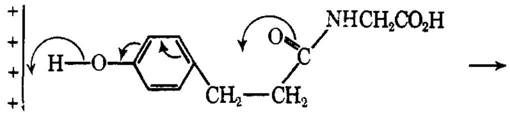


110

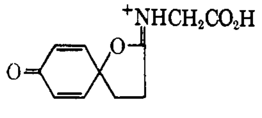


111

Intramolecular cyclization of *p*-hydroxyphenylpropionic acid derivatives represents a novel method for anodic cleavage of tyrosyl-peptide bonds (122, 384, 706). Electrooxidation of phloretic acid (**112**), for example, leads to the spirodienone **114** and glycine (Eq 62 and 63). A considerable quantity of the 4-hydroxydienone **115** is formed in a competing reaction.



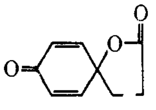
112



$+ H^+ + 2e$ (Eq 62)

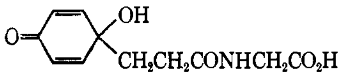
113

113 + H_2O →



$+ H_2NCH_2CO_2H + H^+$ (Eq 63)

114



115

Electrolysis of phenols in basic solution favors formation of dehydrogeno dimers. Corypalline (**116**) electrolyzed under cpe conditions gives a 28% yield of the dimer **117** (59). The same product could be obtained by photolysis of **116** in aqueous alkaline solution, providing a further example of the strong similarity between photochemical and electrochemical oxidations of phenols (394). In basic solution, vanillate anion **118** has been shown to undergo a reversible one-electron transfer to the phenoxy radical **119** which may dimerize to dehydrodivanillin (**120**) (Eq 64 and 65) (808).

Fast-sweep electrochemical techniques applied to the study of oxidation pathways of catecholamines have permitted Adams and coworkers (341) to positively identify the transient intermediates and determine the rates of intramolecular cyclization to the substituted indole. In 1.0 *M* H_2SO_4, the adrenaline (**121**)–adrenalinequinone (**122**) system (Eq 66) has been established by cyclic voltammetry. At pH 3, however, sufficient unprotonated quinone **123** is available to allow the intramolecular 1,4-addition reaction (Eq 66–68) to occur to give leucoadrenochrome (**124**) and adrenochrome (**125**). Since **124** is more easily oxidized than adrenaline itself, **124** is oxidized by 122 to adrenochrome (**125**) and adrenaline (Eq 69). Other catecholamines

Table XI

Oxidation of Phenols and Aminophenols

Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
Phenol			
(a) (H_2O, H_2SO_4)	PbO_2, C	Hydroquinone, benzoquinone, maleic acid, catechol, catechol monophenyl ether, 2,4'-dihydroxybiphenyl, 4,4'-dihydroxybiphenyl, $HOC_{12}H_8OC_{12}H_8$-OH	212, 261, 711
(b) (H_2O, NH_4SCN)	C	*p*-Thiocyanophenol (67)	348, 539, 673
(c) (H_2O, HBr)	Pt	Brominated phenols including tribromophenol	467, 574, 872
(d) (Alkali metal salt)	C, Cu, Zn, Fe	Polymeric film	534
o-Cresol			
(a) (H_2O, H_2SO_4)	PbO_2	2-Methylhydroquinone (2.3 g/20 gsm), 2-methylbenzoquinone, mesaconic acid, 3,3'-dimethyl-4,4'-dihydroxybiphenyl	207, 261
(b) (Concd alkali mixture)	Cu, PbO_2	Salicylic acid	33, 636
(c) (Pyridine, AgCN)	Pt, Ta	Oxamidine derivative	699
(d) (H_2O, NH_4SCN)	C	*p*-Thiocyano-*o*-cresol (72)	348, 539, 673
m-Cresol			
(a) (H_2O, H_2SO_4)	PbO_2	2-Methylhydroquinone, 2-methylbenzoquinone, benzoquinone	207
(b) (H_2O, NH_4SCN)	C	4-Thiocyano-3-methylphenol	539
p-Cresol			
(a) (H_2O, H_2SO_4)	PbO_2	3,3'-Dimethyl-2,2'-dihydroxybiphenyl, 2,2'-dihydroxy-5,5'-dimethyldiphenyl, ether	207
(b) (H_2O, C_2H_5OH, HCl, NaSCN)	C	2-Thiocyano-4-methylphenol	539
2,4-Dimethylphenol (H_2O, H_2SO_4)	PbO_2	2,2'-Dihydroxy-3,5,3',5'-tetramethylbiphenyl, 2,4-dimethyl-4-hydroxy-2,5-cyclohexadienone	232
3,5-Dimethylphenol (H_2O, H_2SO_4)	PbO_2	2,6-Dimethylbenzoquinone (35), di-*m*-xylenol	241
Thymol			
(a) (H_2O, H_2SO_4)	PbO_2	2-Isopropyl-5-methylhydroquinone (7.1), dithymol (6.2)	241, 261
(b) (H_2O, NH_4SCN)	C	4-Thiocyano-2-isopropyl-5-methylphenol (76)	539
Carvacrol (H_2O, NH_4SCN)	C	4-Thiocyano-3-isopropyl-6-methylphenol (50)	539
3,5-Diethylphenol (H_2O, NH_4SCN)	C	4-Thiocyano-3,5-diethylphenol (82)	539
2,4,6-Trichlorophenol (H_2O, H_2SO_4)	Pt	2,6-Dichlorohydroquinone (1.6 g/20 gsm)	261
Salicylic acid (liq NH_3)	Pt	N_2, recovered starting material	317
Phenol-2,4-disulfonic acid[f] (H_2O)	Pt	3,4-Dihydroxybenzenesulfonic acid, benzoquinone	210
Phenol-2,5-disulfonic acid[f] (H_2O)	Pt	CO_2, H_2O, H_2SO_4	210
o-Hydroxyacetophenone (H_2O, CH_3OH, NaOH)	Pt	4,4'-Dihydroxy-3,3'-diacetylbiphenyl (7)	391
p-Hydroxyacetophenone (H_2O, CH_3OH, NaOH)	Pt	No dehydrogeno dimer	391
5-Methyl-2-hydroxyacetophenone (H_2O, CH_3OH, NaOH)	Pt	2,2'-Dihydroxy-3,3'-diacetyl-5,5'-dimethylbiphenyl (26)	391
5-Methyl-2-hydroxybenzophenone (H_2O, CH_3OH, NaOH)	Pt	2,2'-Dihydroxy-3,3'-dibenzoyl-5,5'-dimethylbiphenyl (17)	391
2,6-Dihydroxyacetophenone (H_2O, CH_3OH, NaOH)	Pt	2,4,2',4'-Tetrahydroxy-3,3'-diacetylbiphenyl (52)	391
Vanillin (CH_3CN, $NaClO_4$, $(C_2H_5)_4NOH$)	Pt	Dehydrodivanillin (65.4)	808
2,6-Di-*t*-butyl-*p*-cresol (CH_3CN, $NaClO_4$, $(C_2H_5)_4NOH$, CH_3OH[b])	Pt	2,6-Di-*t*-butyl-4-methyl-4-methoxy-2,5-cyclohexadienone (65.3), 2,6-di-*t*-butyl-1,4-benzoquinone (10.4)	808
2,4,6-Triphenylphenol (H_2O, HOAc, NaOAc), cpe	C	2,4,6-Triphenyl-2-acetoxy-3,5-cyclohexadienone (very good)	151, 740
Hydroquinone			
(a) (H_2O, H_2SO_4)	C, Pt	Quinhydrone (75)	183, 207, 321, 329, 486, 712
(b) (C_5H_5N, $LiClO_4$), cpe 0.30 V *vs.* Ag, Ag^+ (1.0 *M*)	C	2-Pyridinium hydroquinone perchlorate	791
Resorcinol (H_2O, NaSCN)	C	4-Thiocyano-1,3-dihydroxybenzene (50–60)	348, 673
Catechol (H_2O, H_2SO_4)	Pt, PbO_2, Hg	*o*-Benzoquinone, polymer	154, 207, 722
Guaiacol			
(a) (H_2O, H_2SO_4)	PbO_2	Catechol, fumaric acid, 3,3'-dimethoxy-4,4'-dihydroxybiphenyl, CO_2	215
(b) (H_2O, C_2H_5OH, HCl, NH_4SCN)	C	4-Thiocyano-2-methoxyphenol (20.7)	248, 539
Propylguaiacol (H_2O, $NaHCO_3$)	PbO_2	Dipropylguaiacol	213
3-Methoxyphenol (H_2O, H_2SO_4)	PbO_2	2,2'-Dimethoxy-4,4'-dihydroxybiphenyl, resorcinol, succinic acid	215
4-Methoxyphenol (H_2O, H_2SO_4)	PbO_2, C paste[a]	Benzoquinone (quant), CH_3OH	215, 340

TABLE XI (*Continued*)

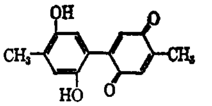
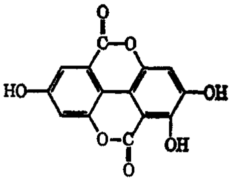
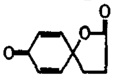
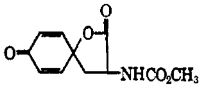
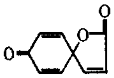
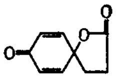
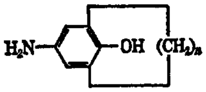
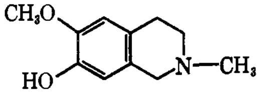
Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
2-Methylhydroquinone (HOAc, H_2SO_4)	Pt		242
2-Methoxy-4-*n*-propylphenol (H_2O, $NaHCO_3$)	PbO_2	Di-*n*-propylguaiacol, higher condensation products	213
Isoeugenol (H_2O, NaOH)	PbO_2	Vanillin (14)	213, 507
Lignosulfonic acid (H_2O, NaCl, thiocyanate)	C	Thiocyanated product	704
Potassium isoeugenolsulfonate (H_2O, Na_2CO_3)	PbO_2	Vanillin (50.1), vanillic acid (4.3), divanillic acid (20.5)	213, 241
3,4-Dihydroxybenzoic acid (H_2O, H_2SO_4)	Pt	Catellagic acid	625
3,5-Dihydroxybenzoic acid (H_2O, H_2SO_4)	Pt		23
2,5-Dihydroxyphenylacetic acid (H_2O, base)[a]	. . .	*p*-Benzoquinoneacetic acid	19
4-Methylcatechol			
(a) (H_2O, $HClO_4$)[c]	C paste	4-Methyl-*o*-benzoquinone	3, 154
(b) (H_2O, HCl)[c]	C paste	5-Chloro-4-methylcatechol	3
1,2,3-Trihydroxybenzene (H_2O, Na_2SO_4)	Pt–Ir, Hg	Purpurogallin (37–45)	154, 622–625
Gallic acid			
(a) (H_2O, NaOAc)	Pt	Purpurogallincarboxylic acid (34)	623–625
(b) (H_2O, H_2SO_4)	Pt	Flavellagic acid	623–625
3-(*p*-Hydroxyphenyl)propionic acid (H_2O)[e]	Pt	 (20)	706
N-Carbomethoxytyrosine (H_2O)[e]	Pt	 (15)	706
p-Hydroxy-*cis*-cinnamic acid (H_2O)[e]	Pt	 (5)	706
Phloretylglycine (H_2O, $(C_2H_5)_4NOAc$, $(C_2H_5)_4NO_2CCF_3$)	Pt	 (30–50), glycine (30–50), 	122, 384
N-Benzoyl-3-nitrotyrosylalanine (H_2O, $(C_2H_5)_4NOAc$, $(C_2H_5)_4NO_2CCF_3$	Pt	Alanine (25–35)	384
Alanylleucine (H_2O, $(C_2H_5)_4NOAc$, $(C_2H_5)_4NO_2CCF_3$)	Pt	No reaction	384
Rufomycin A (H_2O, $(C_2H_5)_4NOAc$, $(C_2H_5)_4NO_2CCF_3$)	Pt	Peptide cleavage (38)	384
Angiotensin amide (H_2O, $(C_2H_5)_4NOAc$, pH 3–5)	Pt	Aspartic acid (from histidine moiety)	122
α-Naphthol			
(a) (H_2O, H_2SO_4)	PbO_2	1,4-Dihydroxynaphthalene, 1,4-naphthoquinone, phthalic acid, α,α'-dinaphthol, ($C_{10}H_7OH + C_{10}H_6O_2$)	604
(b) (H_2O, $NaNO_2$)	C	β-Nitroso-α-naphthol (54.9)	184
β-Naphthol (H_2O, $NaNO_2$)	C	3-Nitroso-2-naphthol (53.8)	184
2-Methyl-1,4-naphthoquinol 1-phosphate (H_2O, H_2SO_4)[a]	C paste	2-Methyl-1,4-naphthoquinone	96
1-Naphthol-4-sulfonic acid (H_2O, $NaNO_2$, NaOAc)	C	2,4-Dinitro-1-hydroxynaphthalene	185
9-Chloro-10-hydroxyanthracene (liq NH_3)	Pt	Recovered starting material, N_2, 9-chlorophenanthryl 9-peroxide (1)	317
Monohalogenated 9,10-dihydroxyanthracenes (H_2O, C_2H_5OH, NaOH)	Hg[d]	Corresponding anthraquinones	565
Phenolphthalein (H_2O, KI, NaOH)	. . .	Tetraiodophenolphthalein	103
Fluorescein			
(a) (H_2O, KBr, NaOH)	Pt	Eosine	734
(b) (H_2O, KI, NaOH)	Pt	Erythrosine	734
2,2,5,7,8-Pentamethyl-6-hydroxychroman (H_2O, pH 3.56)	Hg[d]	2,3,5-Trimethyl-6-(3-hydroxy-3-methylbutyl)benzoquinone	727
p-Aminophenol (H_2O, pH 1.2)[a]	Pt	Benzoquinone, NH_3	732, 778
3,5-Di-*t*-butyl-4-aminophenol (CH_3CN, $LiClO_4$), cpe 0.8 V *vs.* Ag, Ag^+ (0.01 *M*)	Pt	3,5-Di-*t*-butyl-4-imino-2,5-cyclohexadienone (quant)	93

Table XI (*Continued*)

Adrenaline (H_2O, H_2SO_4)[a]			
(a) pH <3	C paste, Pt	Adrenalinequinone,	341
(b) pH 3	C paste, Pt	Leucoadrenochrome, 5,6-dihydroxy-N-methylindole	341
 $(CH_2)_n$ (H_2O, C_2H_5OH, HOAc)[d] $n = 9–19$	Hg	Corresponding benzoquinone	645
Corypalline (H_2O, $NaHCO_3$), cpe 0.7 V *vs.* sce	Pt	N,N′-Dimethyl-6,6′-dimethoxy-7,7′-dihydroxy-1,1′,2,2′,3,3′,4,4′-octahydro-8,8′-biisoquinoline (28)	59
8-Hydroxyquinoline			
(a) (H_2O, KI, Na_2CO_3)	Pt	7-Iodo-8-hydroxyquinoline (68)	78
(b) (H_2O, KI, Na_2CO_3)	Pt	5,7-Diiodo-8-hydroxyquinoline (82.4)	78
(c) (H_2O, HCl, NH_4SCN)	C	5-Thiocyano-8-hydroxyquinoline	539
2-Hydroxyphenothiazine (H_2O, $HClO_4$)	Pt	2-Phenothiazone	51

[a] Electrochemical kinetic study. [b] Gradually added. [c] Cyclic voltammetric study. [d] Polarographic study. [e] Electrolyte unspecified. [f] Ammonium salt.



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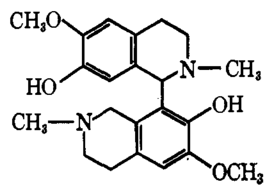

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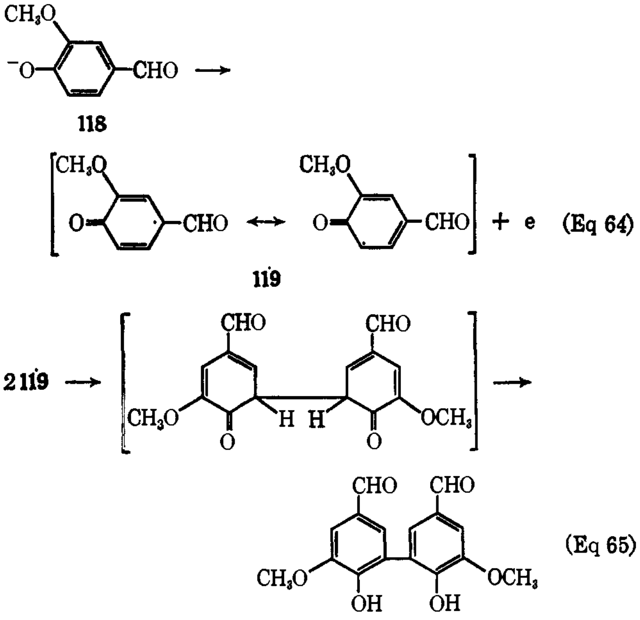
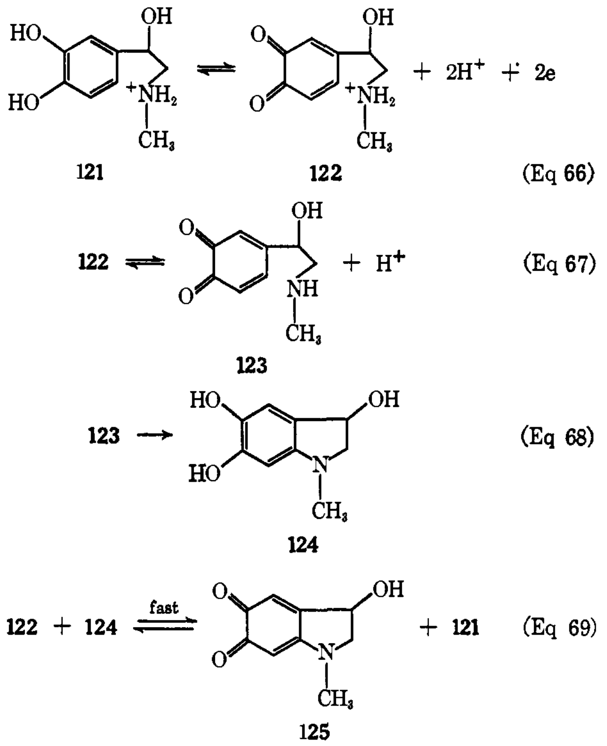




examined include noradrenaline, α-methylnoradrenaline, dopamine, and isoproterenol. Chronoamperometry was used for determination and comparison of their rates of cyclization.

E. OXIDATION OF ESTERS, β-DIKETONES, α-HYDROXY KETONES, OXIMES, AND NITROALKANES (TABLE XII)

The oxidation of salts of carboxylic esters produces dimeric compounds. The mechanism of the reaction probably follows the scheme shown in Eq 70–72 for the electrolysis of diethyl sodiocyanomalonate in aqueous medium. Here the radicals formed in the discharge of carbanions undergo coupling to tetraethyl 1,2-dicyano-1,1,2,2-ethanetetracarboxylate (**126**). The parallel chemical dimerization of such radicals has been well established (17, 419, 420). The reaction is not favored with esters of low acidity and is inhibited when the acidity of the ester approaches that of the solvent

$$NaCCN(CO_2C_2H_5)_2 \rightleftharpoons Na^+ + NC\bar{C}(CO_2C_2H_5)_2 \qquad \text{(Eq 70)}$$

$$NC\bar{C}(CO_2C_2H_5)_2 \rightarrow NC\dot{C}(CO_2C_2H_5)_2 + e \qquad \text{(Eq 71)}$$

$$2NC\dot{C}(CO_2C_2H_5)_2 \rightarrow \begin{array}{l} NCC(CO_2C_2H_5)_2 \\ \quad | \\ NCC(CO_2C_2H_5)_2 \\ \quad \mathbf{126} \end{array} \qquad \text{(Eq 72)}$$

TABLE XII

OXIDATION OF ESTERS, β-DIKETONES, α-HYDROXY KETONES, OXIMES, AND NITROALKANES

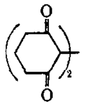
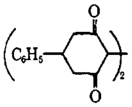
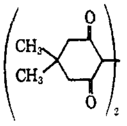
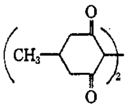
Esters	Anode	Product(s) (% yield)	Ref
Ethyl sodioacetoacetate (C_2H_5OH)	Pt	CH_3CHO, diethyl 4-methyl-2,6-dioxoheptane-3,5-dicarboxylate,[a] further condensation products of CH_3CHO–ethyl acetoacetate[a]	56, 57, 569, 600, 601, 824
Ethyl acetoacetate (CH_3CN, KI)	Pt	Diethyl α,α′-diacetylsuccinate (1.5 g/A hr)	601
Diethyl sodiomalonate (C_2H_5OH)	Pt	1,1,2,2-Tetracarbethoxyethane (1.4 g/A hr), tetraethyl 2-methylpropane-1,1,3,3-tetracarboxylate	56, 58, 569, 600, 601
Diethyl malonate (CH_3CN, KI)	Pt	1,1,2,2-Tetracarbethoxyethane (2.1 g/A hr)	601
Diethyl sodiomethylmalonate (C_2H_5OH)	Pt	2,2,3,3-Tetracarbethoxybutane (2)	824
Diethyl sodioethylmalonate (C_2H_5OH)	Pt	3,3,4,4-Tetracarbethoxyhexane (2)	824
Ammonium diethylnitromalonate (H_2O)	Pt	1,2-Dinitro-1,1,2,2-tetracarbethoxyethane	794
Diethyl sodiocyanomalonate (H_2O)	Pt	Tetraethyl 1,2-dicyano-1,1,2,2-ethanetetracarboxylate (21)	795
Ethyl cyanoacetate			
(a) (C_2H_5OH, KI)	Pt	Diethyl α,α′-dicyanosuccinate	603
(b) (DMF, KI)	Pt	N,N-Dimethylcyanoacetamide, diethyl α,α′-dicyanosuccinate, $C_2H_5O_2C(CN){=}C(CN)CO_2C_2H_5$	603
(c) (CH_3CN, KI)	Pt	$C_2H_5O_2C(CN){=}C(CN)CO_2C_2H_5$	603
Sodium triethyl methanetricarboxylate (H_2O)	Pt	Hexaethyl ethanehexacarboxylate (40)	4, 569
Ethyl sodiophenylacetate (C_2H_5OH)	Pt	Diethyl α,α′-diphenylsuccinate (trace)	601
Ethyl phenylacetate (CH_3CN, KI)	Pt	Diethyl α,α′-diphenylsuccinate (2.3 g/A hr)	601
Ethyl α-cyanophenylacetate (CH_3OH or C_2H_5OH, I_2, KI)	Pt	Diethyl 1,2-dicyano-1,2-diphenylsuccinate α,α′-diphenylsuccinonitrile	602
Sodium 4,4-dicarbethoxybutadien-1,3-olate (DMF, $LiClO_4$), cpe 0.9 V *vs.* Hg, Hg^{2+} (0.01 *M*)	Pt	$(C_2H_5O_2C)_2C{=}CH\dot{C}H{-}CHO$ (quant)[a]	304
		β-Diketones	392, 569
Acetylacetone (H_2O, NaOH)	Pt	Tetraacetylethane (11)	
Cyclohexane-1,3-dione (H_2O, NaOH)	Pt	 (20)	392
5-Phenylcyclohexane-1,3-dione (H_2O, CH_3OH, NaOH)	Pt	 (20)	392
5,5-Dimethylcyclohexane-1,3-dione (H_2O, CH_3OH, NaOH)	Pt	 (30)	392
5-Methylcyclohexane-1,3-dione (H_2O, CH_3OH, NaOH)	Pt	 (50)	392
		α-Hydroxy Ketones	
Benzoin			
(a) (H_2O, acetone, H_2SO_4)	Pt	Benzil (0.5 g/15 gsm), benzaldehyde (4.6 g)	471
(b) (H_2O, C_2H_5OH, NaOH, or saturated aqueous sodium xylenesulfonate)	Pt	Benzoic acid (60)	387, 532, 533
(c) (H_2O, C_2H_5OH, HCl)	Pt	Benzil (75.4)	387
p,p′-Diisopropylbenzoin (H_2O, acetone, H_2SO_4)	Pt	*p*-Isopropylbenzaldehyde (3.3 g/100 gsm), *p*-isopropylbenzoic acid (3.5 g)	471
Furoin (H_2O, pyridine, H_2SO_4)	Pt	Furil (3 g/10 gsm)	471
Benzofuroin (H_2O, acetone, H_2SO_4)	Pt	Benzoic acid (3.2 g/10 gsm)	471
2,2′-Pyridoin (H_2O, C_2H_5OH, NaOH)	Hg	2,2′-Pyridil	359
Ascorbic acid Coumarindiol Dihydroxyacrylic acid Dihydroxyfumaric acid Hydroxypyruvic acid	polarographic studies at Hg in aqueous media	Corresponding α-diketone (hydrated)	74, 282, 283, 385
		Oximes	
Sodium diethyl oximinomalonate (H_2O)	Pt	*sym*-Dinitrosotetracarbethoxyethane	796
Potassium ethyl α-oximinopropionate (H_2O)	Pt	Diethyl 1,2-dinitroso-1,2-dimethylsuccinate	796
Potassium ethyl α-oximinobutyrate (H_2O)	Pt	Diethyl 1,2-dinitroso-1,2-diethylsuccinate	796
Acetoxime (H_2O, H_2SO_4)	Pt	2-Nitro-2-nitrosopropane	714

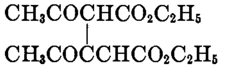
TABLE XII (*Continued*)

Nitroalkanes	Anode	Product(s) (% yield)	Ref
		Nitroalkanes	
Nitromethane (H_2O, $(C_2H_5)_3N$)	Pt	2-Nitroethanol (25), HCHO	620
Nitroethane			
(a) (H_2O, NaOH)	Pt	2-Nitro-2-butene, 2,3-dinitrobutane	27
(b) (H_2O, $(C_2H_5)_3N$)	Pt	3-Nitro-2-butanol (25)	620
(c) (H_2O, KNO_2), cpe <0.70 V *vs.* sce	Ag	1,1-Dinitroethane (82)	855
(d) (H_2O, KNO_2)	Fe, Ni, C, Pt	1,1-Dinitroethane (30), ethylnitrolic acid	855
(e) (H_2O, NaOH, $NaNO_2$)	Pt	1,1,1-Trinitroethane	337
(f) (H_2O, NaN_3)	Pt	1-Azido-1-nitroethane	856
1,1-Dinitroethane			
(a) (H_2O, NaOH)	Pt	2,2,3,3-Tetranitrobutane	337
(b) (H_2O, NaOH, $NaNO_2$)	Pt	1,1,1-Trinitroethane (8.5)	337
1-Nitropropane			
(a) (H_2O, NaOH)	Pt	3,4-Dinitrohexane (25–30), 3-nitro-3-hexene (45–55), 3,4,5-trinitro-4-ethylheptane	27
(b) (H_2O, NaN_3)	Pt	1-Azido-1-nitropropane	856
1,1-Dinitropropane (H_2O, NaOH, $NaNO_2$)	Pt	1,1,1-Trinitropropane (20)	337
2-Nitropropane			
(a) (H_2O, NaOH)	Pt, C	2,3-Dinitro-2,3-dimethylbutane (15), 2,2-dinitropropane	28, 620, 873
(b) (H_2O, $(C_2H_5)_3N$)	Pt	Acetone (50)	620
(c) (H_2O, NaOH, $NaNO_2$)	Pt	2,2-Dinitropropane	28
(d) (H_2O, NaN_3)	Pt	2-Azido-2-nitropropane	856
1-Hydroxy-2-nitropropane (H_2O, NaN_3)	Pt	1-Hydroxy-2,2-diazidopropane	856
1-Nitrobutane (H_2O, NaOH)	Pt	4-Nitrooctene (35), 4,5-dinitrooctane (35)	27
2-Nitrobutane			
(a) (H_2O, NaOH)	Pt	3,4-Dinitro-3,4-dimethylhexane (70), 2,2-dinitrobutane (20)	28
(b) (H_2O, NaOH, $NaNO_2$)	Pt	3,4-Dinitro-3,4-dimethylhexane (15–20), 2,2-dinitrobutane (70–80)	28
1,1-Dinitrobutane (H_2O, NaOH, $NaNO_2$)	Pt	1,1,1-Trinitrobutane (18)	337
1-Nitrohexane (H_2O, NaN_3)	Pt	1-Azido-1-nitrohexane	856
Nitrocyclohexane			
(a) (H_2O, NaN_3)	Pt	1-Azido-1-nitrocyclohexane (89)	856
(b) (H_2O, NaOH, $NaNO_2$)	Pt	Cyclohexanone (3 g/64.2 gsm), 1,1′-dinitrodicyclohexyl (5 g), 1,1-dinitrocyclohexane (15 g)	28

[a] Isolated as the 2,4-dinitrophenylhydrazone derivative.

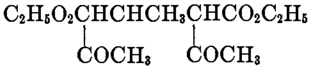
(usually water or aqueous alcohol). It would be interesting in this respect to extend the scope of these reactions by employing aprotic solvents.

The formation of dimer in the electrolysis of ethyl sodioacetoacetate, reported earlier, has been questioned recently by Binns and Brettle (57). These authors find no coupled ester **127** in either 5% aqueous ethanol or absolute ethanol, but instead, acetaldehyde and diethyl 4-methyl-2,6-dioxoheptane-3,5-dicarboxylate (**128**). It is probably the carbanion **129** which is discharged anodically in this process since it has been demonstrated spectroscopically that ethyl acetoacetate with 1 equiv of sodium alkoxide in ethanol is entirely converted to the anion (42). Acetaldehyde could then be produced by radical abstraction of hydrogen from the alcohol according to the proposed scheme (Eq 73–75). Reaction of acetaldehyde with ethyl acetoacetate affords the condensation product **128**.



$$\begin{array}{l}\mathrm{CH_3COCHCO_2C_2H_5}\\ \qquad\quad |\\ \mathrm{CH_3COCCHCO_2C_2H_5}\end{array}$$

127



$$\mathrm{C_2H_5O_2C\underset{\substack{|\\ \mathrm{COCH_3}}}{C}HCH\,CH_3\underset{\substack{|\\ \mathrm{COCH_3}}}{C}HCO_2C_2H_5}$$

128

$$\underset{\mathbf{129}}{\mathrm{CH_3COCHCO_2C_2H_5}} \rightarrow \mathrm{CH_3CO\dot{C}HCO_2C_2H_5} + e \qquad \text{(Eq 73)}$$

$$\mathrm{CH_3CO\dot{C}HCO_2C_2H_5 + CH_3CH_2OH \rightarrow CH_3\dot{C}HOH + CH_3COCH_2CO_2C_2H_5} \qquad \text{(Eq 74)}$$

$$\mathrm{2CH_3\dot{C}HOH \rightarrow CH_3CHO + CH_3CH_2OH} \qquad \text{(Eq 75)}$$

A novel method has been developed recently by Okubo and Tsutsumi whereby higher yields of coupling products may be realized (601). Indeed, application of this procedure, which involves electrooxidation of the ester in CH_3CN containing potassium iodide, provides a reasonable yield of the dimer **127** from ethyl acetoacetate. The success of this method is due in large part to minimal cooxidation of solvent, while the discharge of iodide ion to iodine (Eq 76) assures a relatively low anodic working potential. The cation is simultaneously reduced to potassium metal which reacts with the ester to give ethyl potassioacetoacetate (**130**) (Eq 77 and 78). The salt **130** may then react with the anodically generated iodine to yield the dimer

$$\mathrm{I^-} \xrightarrow{-e} \mathrm{I\cdot} \rightarrow {}^1/_2\mathrm{I_2} \qquad \text{(Eq 76)}$$

$$\mathrm{K^+} + e \rightarrow \mathrm{K\cdot} \qquad \text{(Eq 77)}$$

$$\mathrm{K\cdot + CH_3COCH_2CO_2C_2H_5 \rightarrow} \underset{\mathbf{130}}{\mathrm{[CH_3COCHCO_2C_2H_5]^-K^+}} + {}^1/_2\mathrm{H_2} \qquad \text{(Eq 78)}$$

$$2(\mathbf{130}) + \mathrm{I_2} \rightarrow 2\mathrm{KI} + \mathbf{127} \qquad \text{(Eq 79)}$$

127 in a manner quite analogous to the known chemical coupling of similar salts with iodine (Eq 79) (95).

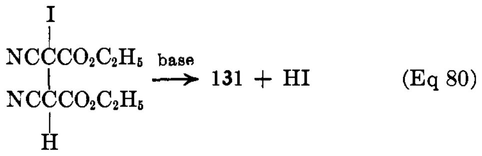
While electrolysis of ethyl cyanoacetate is reported to give the expected dimer in ethanolic potassium iodide solution, the reaction in DMF or CH_3CN affords the olefin **131** in addition (603). A third product, N,N-dimethylcyanoacetamide (**132**), is formed in DMF. The preparation of **131** in aprotic media was interpreted in terms of coupling of the carbene intermediate **133**. An alternative scheme may be more plausible: dehydrohalogenation of the iodinated cyanoacetic ester dimer **134** (Eq 80).

$$NCC(CO_2C_2H_5){=}CCN(CO_2C_2H_5) \qquad NCCH_2CON(CH_3)_2$$

131 **132**

$$NC\ddot{C}CO_2C_2H_5$$

133



$$NC\overset{I}{C}CO_2C_2H_5 - NC\underset{H}{C}CO_2C_2H_5 \xrightarrow{\text{base}} 131 + HI \qquad \text{(Eq 80)}$$

134

An interesting example of electrochemical ester coupling has provided additional evidence for the formation of radicals in the discharge step (304). The ester **135** exists in the enolic form **136** in aqueous solution above pH 4.7. On oxidation of **136** (in DMF under cpe conditions), one electron is transferred per molecule, and the product formed is the relatively stable free radical **137** (Eq 81 and 82). Work-up of the electrolysate and treatment with 2,4-dinitrophenylhydrazine gave a nonconjugated (uv) derivative which possessed an esr signal without fine structure. The authors propose that the product is the monomeric free radical 137 (as the 2,4-dinitrophenylhydrazone derivative) in equilibrium with its dimer. The site of coupling could not be verified although structure **138** is probably correct.

$$(C_2H_5O_2C)_2CHCH{=}CHCHO + NaOH \xrightleftharpoons{H_2O}$$

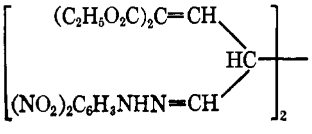
135

$$(C_2H_5O_2C)_2C{=}CHCH{=}C\bar{O}H\ Na^+ + H_2O \qquad \text{(Eq 81)}$$

136

$$136 \xrightarrow{-e} [(C_2H_5O_2C)_2\dot{C}CH{=}CHCHO \longleftrightarrow (C_2H_5O_2C)_2C{=}CH\dot{C}HCHO \updownarrow (C_2H_5O_2C)_2C{=}CHCH{=}CHO\cdot] \qquad \text{(Eq 82)}$$

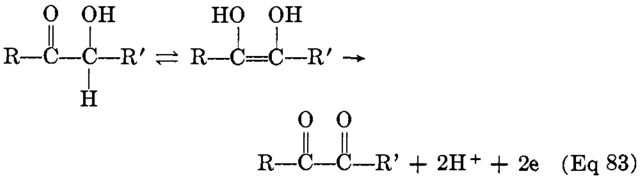
137



138

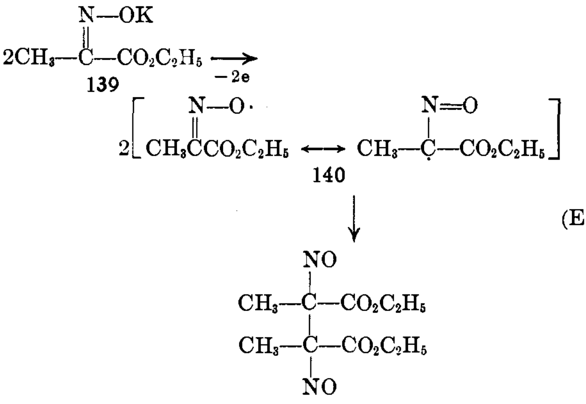
The dimerization of β-diketones produces fair to good yields of the corresponding dehydrogeno dimers. The mechanism appears to be similar to that of the ester coupling reaction.

The electrooxidation of α-hydroxy ketones (enediols or acyloins) has been studied in aqueous media and has been the subject of a number of polarographic investigations. In general these compounds can undergo oxidative fission to give a mixture of carboxylic acid and aldehyde or upon milder oxidation afford the corresponding α-diketone. Both types of reaction have been observed chemically (667, 668). Polarographic studies of enediols have demonstrated that α-diketones are formed in a two-electron per molecule oxidation (Eq 83) (74, 358, 359).



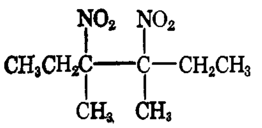
$$R{-}\overset{O}{\overset{\|}{C}}{-}\underset{H}{\overset{OH}{C}}{-}R' \rightleftharpoons R{-}\overset{HO}{C}{=}\overset{OH}{C}{-}R' \rightarrow R{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}R' + 2H^+ + 2e \qquad \text{(Eq 83)}$$

No further work has appeared on oxidative dimerization of oximino salts of α-ketoesters since the original papers of Ulpiani and Rodano (796, 797). As an example, the electrolysis of the potassium salt of ethyl pyruvate oxime (**139**) affords diethyl 1,2-dinitroso-1,2-dimethylsuccinate (**141**), presumably *via* coupling of the resonance-stabilized nitroso radical **140** (Eq 84).



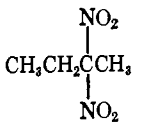
$$2CH_3{-}\overset{N-OK}{\overset{\|}{C}}{-}CO_2C_2H_5 \xrightarrow[-2e]{} 2\left[CH_3\overset{N-O\cdot}{\overset{\|}{C}}CO_2C_2H_5 \longleftrightarrow CH_3{-}\overset{N=O}{\dot{C}}{-}CO_2C_2H_5\right] \rightarrow CH_3{-}\overset{NO}{C}(CO_2C_2H_5){-}\underset{NO}{C}(CO_2C_2H_5){-}CH_3 \qquad \text{(Eq 84)}$$

The electrochemical introduction of geminal nitro and azido groups into nitroparaffins represents a successful method of preparing highly energetic compounds (28, 856). While oxidation of nitroparaffins in aqueous alkaline media produces dimers, *gem*-dinitroparaffins, and often olefinic material, addition of a nitrite salt to the electrolysate increases the proportion of *gem*-dinitroparaffin. For example, electrolysis of 2-nitrobutane in aqueous base at Pt yields a mixture of 3,4-dinitro-3,4-dimethylhexane (**142**) (70%) and 2,2-dinitrobutane (**143**) (20%). On addition of sodium nitrite, the reaction favors the formation of **143** (70–80%) over **142** (15–20%). In the absence of added nitrite the production of *gem*-dinitroparaffins is ac-



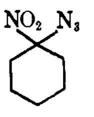
$\mathrm{CH_3CH_2\overset{NO_2}{\underset{CH_3}{C}}-\overset{NO_2}{\underset{CH_3}{C}}-CH_2CH_3}$

142



$\mathrm{CH_3CH_2\overset{NO_2}{\underset{NO_2}{C}}CH_3}$

143

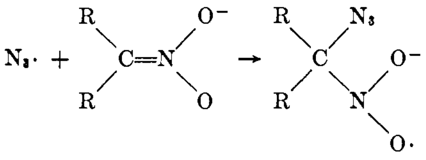


144

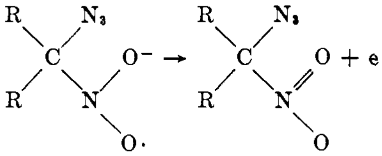
counted for by elimination of nitrite ion from the dimer. The formation of *gem*-dinitroparaffins is almost completely inhibited at a graphite anode. Prolonged electrolysis of nitroethane or 1,1-dinitroparaffins in aqueous alkaline nitrite solution affords 1,1,1-trinitroparaffins in up to 20% yield.

Introduction of the azide function proceeds in an analogous manner (856). Thus electrolysis of nitrocyclohexane in aqueous azide solution at Pt or Ni anodes provides an 89% yield (64% CE) of 1-azido-1-nitrocyclohexane (**144**). These products generally precipitate out of solution as formed. However, if the 1-azido-1-nitroparaffin is soluble (as is the case in the electrolysis of 2-nitropropanol), the nitro group is readily displaced by azide ion in a later chemical reaction, to afford the *gem*-diazido compound. A study of some of the reaction variables has established that the reaction is favored by low pH (pH 10.5 is the lowest achievable before the nitroparaffin becomes almost insoluble) and high azide concentration. Added perchlorate ion reduces the current efficiency, while little effect of current density on the yield of products is apparent. The mechanism has been interpreted in terms of an attack of anodically generated azide radical on nitronate ion. The resultant radical anion undergoes a second electron-transfer step to form the product (Eq 85–87). In support of this scheme is the apparent lack of dimer, expected from discharge of nitronate ion. Furthermore, a solution of sodium azide was found to oxidize at a lower anode potential than a solution of nitrocyclohexane under the same conditions of current density and pH.

$$N_3^- \rightarrow N_3\cdot + e \qquad \text{(Eq 85)}$$

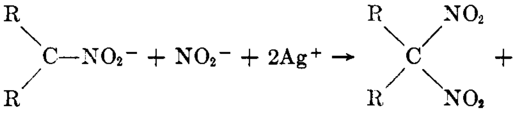


(Eq 86)

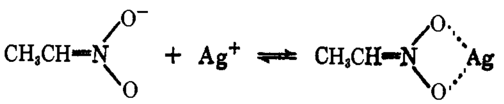


(Eq 87)

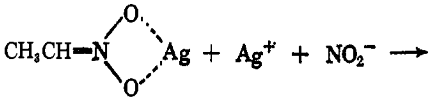
A novel approach to the preparation of *gem*-dinitroparaffins is based on the chemical reaction of nitronate salts with silver and nitrite ions in aqueous solution (Eq 88) (400, 710). The electrochemical method conveniently avoids handling large amounts of silver salt and metal by employing a bed of silver powder as the anode. As the reaction proceeds, the anode is oxidized to silver ions while the silver metal which settles out of solution returns to the anode bed. An unusual cell design permits continuous collection of the insoluble product. Based on their electrochemical studies, Wright and Levering (855) have proposed the formation of a covalently bonded complex **145** (Eq 89–92).



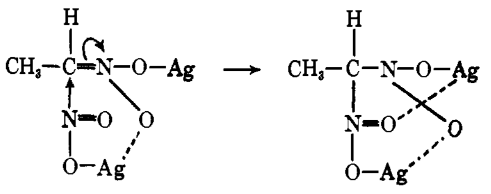
(Eq 88)



(Eq 89)



(Eq 90)

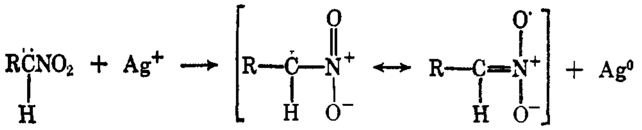


145

(Eq 91)

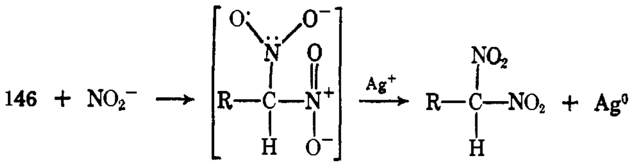
Collapse of the complex is acid catalyzed. An alternative mechanism has been suggested by Kornblum (202). The nitronate and silver ions could combine to give a resonance-stabilized free radical **146**. The latter then reacts with nitrite ion forming the radical anion **147** which is oxidized by a second silver ion to the product and silver metal.

$$\mathbf{145} + H^+ \longrightarrow \text{product} \qquad \text{(Eq 92)}$$



146

(Eq 93)



147

(Eq 94)

F. OXIDATION OF AMIDES AND LACTAMS (TABLE XIII)

A study of the cyclic voltammetry of a number of aliphatic amides in CH_3CN demonstrates that primary amides are oxidized near 2.0 V, secondary amides at 1.8 V, and tertiary amides from 1.2 to 1.5 V *vs.* sce (596). Moreover, in all cases a one-step irreversible oxidation is observed while coulometric analysis re-

TABLE XIII

OXIDATION OF AMIDES AND LACTAMS

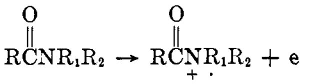
Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
		Hydroxylation (Oxidation in Aqueous Media)	
Formamide (H_2O, H_2SO_4)	Pt	Urea, cyanuric acid (33)	135, 263, 703
Amidosulfonic acid (H_2O, KOH)	Pt	Potassium azidodisulfonate (66)	449
Thiourea (HX, X = Cl, Br, NO_3, $^1/_2SO_4$, or $^1/_2S_2O_6$)	Pt	Formamidine disulfide·2HX	211, 268, 687, 712
sym-Diethylthiourea (H_2O, $HClO_4$)	Pt	Tetraethylformamidine disulfide diperchlorate (45)	211
Allylthiourea (H_2O, HCl)	Pt	Bis-(β,γ-dichloropropyl]formamidine disulfide dihydrochloride (50)	211
N-Methylformamide (H_2O, H_2SO_4)	Pt	2,6-Diaza-4-oxa-1,7-heptanedione	135
N,N-Dimethylformamide			
(a) (H_2O, NH_4NO_3)	Pt	2,6-Diformyl-2,6-diaza-4-oxaheptane (50)	678
(b) (H_2O, H_2SO_4)	Pt	2,6-Dimethyl-2,6-diaza-4-oxa-1,7-heptanedione	678
N-Methylacetamide			
(a) (H_2O, H_2SO_4)	Pt	3,5-Diaza-2,6-heptanedione (13 g/faraday)	678
(b) (CH_3CN, H_2O, $NaClO_4$),[a] cpe 1.35 V *vs.* sce	Pt	Acetamide (76), HCHO (21)	596
N,N-Dimethylacetamide (CH_3CN, H_2O, $NaClO_4$),[a] cpe 1.35 V *vs.* sce	Pt	N-Methylacetamide (49), HCHO (45)	596
N,N-Diethylbutyramide (CH_3CN, H_2O, $NaClO_4$)[a], cpe 1.35 V *vs.* sce	Pt	N-Ethylbutyramide (45), acetaldehyde (36)	596
N-Propylacetamide (CH_3CN, H_2O, $NaClO_4$),[a] cpe 1.60 V *vs.* sce	Pt	Propionaldehyde (31)	596
N,N-Dipropylacetamide (CH_3CN, H_2O, $NaClO_4$)[a]	Pt	N-Propylacetamide (44), propionaldehyde (53)	596
N,N-Diamylacetamide (CH_3CN, H_2O, $NaClO_4$),[a] cpe 1.35 V *vs.* sce	Pt	N-Amylacetamide (52), valeraldehyde (49)	596
N,N-Dipropylpropionamide (CH_3CN, H_2O, $NaClO_4$),[a] cpe 1.35 V *vs.* sce	Pt	N-Propylpropionamide (49), propionaldehyde (38)	596
N-Cyclopropylcyclopropanecarboxamide	...	Cyclopropanecarboxylic acid, NH_3	353
N-Acetyl-β-alanine (H_2O, H_2SO_4)	Pt, PbO_2	Malonic acid (13–16)	556
N-Acetyl-γ-aminobutyric acid			
(a) (H_2O, H_2SO_4)	Pt	Succinic acid (49.4)	556
(b) (H_2O, H_2SO_4)	PbO_2	N-Acetylsuccinamic acid (55)	556
N-Acetyl-ϵ-aminocaproic acid			
(a) (H_2O, H_2SO_4)	Pt	Adipic acid (46.5)	556
(b) (H_2O, H_2SO_4)	PbO_2	Adipamic acid (5.7), adipic acid (13.5)	556
N-Methylsuccinamide (H_2O, H_2SO_4)	PbO_2	HCO_2H (8.4), HCHO (11.3), CO_2 (64), succinic acid (72.3)	557
N-Ethylsuccinamide (H_2O, H_2SO_4)	PbO_2	HOAc (70), acetaldehyde (5), CO_2 (37), succinic acid (76)	557
N-*n*-Propylsuccinamide (H_2O, H_2SO_4)	PbO_2	Propionic acid (53.6), succinic acid (68)	557
N-*n*-Butylsuccinamide (H_2O, H_2SO_4)	PbO_2	*n*-Butyric acid (56.5), succinic acid (82)	557
N-Isobutylsuccinamide (H_2O, H_2SO_4)	PbO_2	Isobutyric acid (42.9), succinic acid (80)	557
N-*n*-Amylsuccinamide (H_2O, H_2SO_4)	PbO_2	*n*-Valeric acid (49.2), succinic acid (84)	557
N-Isopropylsuccinamide (H_2O, H_2SO_4)	PbO_2	Acetone (77.5), succinic acid (76)	557
N-*sec*-Butylsuccinamide (H_2O, H_2SO_4)	PbO_2	Methyl ethyl ketone (42.2), succinic acid (80)	557
N-Acetylethylenediamine (H_2O, H_2SO_4)	Pt, PbO_2	Glycine (54–64)	559
α-N-Acetylpropylenediamine (H_2O, H_2SO_4)	Pt, PbO_2	α-Alanine (21–37.3)	559
N-Acetyltrimethylenediamine (H_2O, H_2SO_4)	Pt, PbO_2	β-Alanine (34.6–75.4)	559
N-Acetylhexamethylenediamine (H_2O, H_2SO_4)	Pt, PbO_2	ϵ-Leucine (44–50)	559
N,N′-Diacetylhexamethylenediamine (H_2O, H_2SO_4)	Pt, PbO_2	ϵ-Leucine (33–51)	559
o-Toluenesulfonamide (H_2O, Na_2CO_3)	PbO_2	Saccharin (78)	159, 229, 335, 594
ϵ-Caprolactam (H_2O, H_2SO_4)	PbO_2	Adipamic acid (13.1), adipic acid (14.8)	560
α-Pyrrolidone (H_2O, H_2SO_4)	PbO_2	Succinimide (59)	560
α-Piperidone (H_2O, H_2SO_4)	PbO_2	Glutarimide (43)	560
Thiobenzamide, thiobenzanilide (see Miscellaneous oxidations)			
		Alkoxylation	
N,N-Dimethylformamide			
(a) (CH_3OH, NH_4NO_3 or $NaOCH_3$)	Pt	N-Methoxymethyl-N-methylformamide (52)	678
(b) (C_2H_5OH, NH_4NO_3)	Pt	N-Ethoxymethyl-N-methylformamide (67)	678
(c) (n-C_4H_9OH, NH_4NO_3)	Pt	N-*n*-Butoxymethyl-N-methylformamide (82)	678
N,N-Dimethylacetamide (n-C_4H_9OH, NH_4NO_3)	Pt	N-*n*-Butoxymethyl-N-methylacetamide (78)	678
N,N-Dimethylbenzamide (C_2H_5OH, NH_4NO_3)	Pt	N-Ethoxymethyl-N-methylbenzamide (54)	678
		Acyloxation	
N,N-Dimethylformamide			
(a) (($C_2H_5)_3N$, $(C_6H_5)_3CO_2H$)	Pt	N-Methyl-N-(triphenylacetoxymethyl)formamide (65), triphenylmethane (3), CO_2 (5.5), CO	654
(b) (HOAc, NH_4NO_3)	Pt	N-Acetoxymethyl-N-methylformamide (54)	677, 678

TABLE XIII (*Continued*)

Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
(c) (HCO_2H, HCO_2K)	Pt	N-Formyloxymethyl-N-methylformamide (69), 2,6-diformyl-2,6-diaza-4-oxaheptane	167, 677, 679
N,N-Dimethylacetamide (HOAc, NaOAc), cpe 1.50 V *vs.* sce	Pt	N-Acetoxymethyl-N-methylacetamide (24)	679
		Miscellaneous	
Formamide (LiCl)	Pt	Cyanuric acid (79)	135
Acetamide (H_2O, NaBr, NaOH)	Pt	N-Acetyl-N-methylurea (67)	466
N-Methylacetamide (anhydrous conditions)	Pt	3,7-Diaza-5-oxa-2,8-nonanedione	135
N,N-Dimethylacetamide			
(a) (H_2SO_4)	Pt	3,5-Dimethyl-3,5-diaza-2,6-heptanedione (30 g/faraday)	135
(b) (CH_3CN, $NaClO_4$),[b] cpe 1.35 V *vs.* sce	Pt	N,N-Dimethylacetamide (95), succinonitrile (85)	596
Ammonium carbamate (liq NH_3, NH_4Cl)	Pt	Azodicarbonamide?[c]	118
Urea (liq NH_3, NaF)	Pt	Azodicarbonamide?[c]	118
Succinimide (H_2O, NaBr, NaOH)	Pt	N-Bromosuccinimide (54)	465

[a] Concentration of water, 199 m*M*. [b] A number of additional amides not listed here undergo the same reaction, *i.e*, recovery of amide and succinonitrile formation. [c] Product isolated as potassium azodicarbonate.

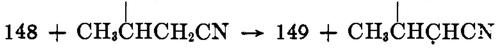
veals a loss of one electron per amide molecule. The products of cpe consist of 90–98% of protonated amide, starting material, and 83–94% of succinonitrile. With isobutyronitrile as solvent, protonated amide and methacrylonitrile are found. The formation of these materials has been interpreted in terms of a mechanism in which amide cation radical **148** generated at the anode abstracts a hydrogen atom from the solvent to form protonated amide **149**. The resultant cyanomethyl radical **150** from CH_3CN or the isopropylcyanomethyl radical **151** from isobutyronitrile undergoes dimerization to succinonitrile or disproportionation to methacrylonitrile and isobutyronitrile, respectively (Eq 95–99). In the presence of increasing water concentration the secondary and tertiary amides provide increasing quantities of dealkylated amide and the corresponding aldehyde. Presumably the cation radical **148** may in addition undergo loss of a proton and electron providing cation **152**, which could react with water to give rise to dealkylated amide and aldehyde (Eq 100 and 101). Since the amide products are protonated and hence protected from further oxidation, only one dealkylation can take place with tertiary amides. Photooxidation of N-pentylhexanamide occurs in an analogous manner with formation of valeraldehyde, valeric acid, and caproic acid (709).



$$R\overset{O}{\overset{\|}{C}}NR_1R_2 \rightarrow R\overset{O}{\overset{\|}{C}}\underset{+\ \cdot}{N}R_1R_2 + e \qquad \text{(Eq 95)}$$

148

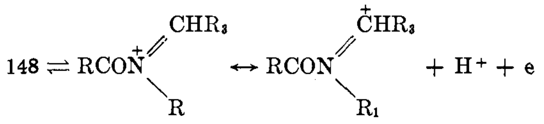
$$148 + CH_3CN \rightarrow \underset{149}{RCO\overset{+}{N}HR_1R_2} + \underset{150}{\cdot CH_2CN} \qquad \text{(Eq 96)}$$



$$148 + CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CN \rightarrow 149 + \underset{151}{CH_3\overset{CH_3}{\overset{|}{C}}\underset{\cdot}{C}HCN} \qquad \text{(Eq 97)}$$

$$2150 \rightarrow (CH_2CN)_2 \qquad \text{(Eq 98)}$$

$$2151 \rightarrow CH_3\overset{CH_3}{\overset{|}{C}}{=}CHCN + CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CN \qquad \text{(Eq 99)}$$



$$148 \rightleftharpoons RCO\overset{+}{N}(=CHR_3)(R) \leftrightarrow RCON(=\overset{+}{C}HR_3)(R_1) + H^+ + e \qquad \text{(Eq 100)}$$

152

$$152 + H_2O \rightarrow RCO\overset{+}{N}H_2R_1 + R_3CHO \qquad \text{(Eq 101)}$$

Electrooxidation of a variety of amides and lactams in aqueous acid media has been studied by Mizuno. The method successfully provides dealkylation products which include carboxylic acids, amino acids, ketones, and imides (556–560).

Both alkoxylation and acyloxylation of N,N-dialkylamides follow a similar course of reaction, forming stable α-substituted products (654, 677–679). On the basis of current–voltage curves, the acetoxylation of DMF probably follows a cation-radical mechanism while on the same basis the mechanism for the formyloxylation reaction remains unclear (167, 678). The alkoxylation of tertiary amides has been interpreted (678) in terms of a reaction of anodically generated nitrate radical or nitrate cation with the amide (hydrogen atom or hydride ion abstraction) since polarization curves showed no change from background on addition of amide. Moreover, NH_4NO_3 gave alkoxylated products in much higher yield than when sodium alkoxides were employed. Examination of the current–voltage curves for $NaOCH_3$ and NH_4NO_3 in CH_3OH demonstrates that the latter system is oxidized at about 0.5 V more anodically than the former, implying that, in the more acidic NH_4NO_3 solution containing amide, the cooxidation of electrolyte or solvent will be relatively less significant than electrooxidation of amide. Thus without further evidence to the contrary a cation-radical mechanism appears reasonable (832).

G. OXIDATION OF ALIPHATIC AND AROMATIC HALIDES (TABLE XIV)

Aliphatic iodides in CH_3CN solution are oxidized potentiostatically to N-alkylacetamides and iodine by a Ritter-like reaction (669) involving alkylcarbonium

Table XIV

Oxidation of Aliphatic and Aromatic Halides

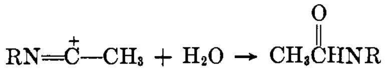
Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
Methyl iodide			
(a) (CH_3CN, $LiClO_4$), cpe 1.9 V *vs.* Ag, Ag^+ (0.01 *M*)	Pt	N-Methylacetamide (75), acetamide (trace), CH_3OH (trace), I_2 (92)	551
(b) (AlI_3)	Al	Methylaluminum diiodide	94
Isopropyl iodide (CH_3CN, $LiClO_4$), cpe 1.95 V *vs.* Ag, Ag^+ (0.01 *M*)	Pt	Dibromopropene[a]	551
Neopentyl iodide (CH_3CN, $LiClO_4$), cpe 1.9 V *vs.* Ag, Ag^+ (0.01 *M*)	Pt	N-*t*-Pentylacetamide (16–21), acetamide, I_2 (100)	551
Iodobenzene			
(a) (H_2O, H_2SO_4)[b]	PbO_2	Hydroquinone, I_2	228
(b) (H_2O, H_2SO_4)	Pt	Quinone, iodic acid, CO_2, fumaric acid	228
(c) (HOAc, H_2SO_4)	Pt	Iodoxybenzene (20), iodosobenzene	228
(d) (HOAc, H_2SO_4)[c]	Pt	Iodosobenzene diacetate	228
(e) (HOAc, $HClO_4$)	Pt	Iodosobenzene, *p*-diiodobenzene	228
(f) (HOAc, NaOAc), cpe 1.75 V *vs.* sce	Pt	Iodoxybenzene,[d] *o*-, *m*-, and *p*-acetoxyiodobenzene	164
(g) (CH_3CN, AgF)	Pt	Iodobenzene difluoride	700
(h) (CH_3CN, $LiClO_4$), cpe 1.65 V *vs.* Ag, Ag^+ (0.01 *M*)	Pt	4-Iododiphenyliodonium perchlorate (45)	551
(i) (CH_3CN, benzene, $LiClO_4$), cpe 1.65 V *vs.* Ag, Ag^+ (0.01 *M*)	Pt	Diphenyliodonium perchlorate (44)	551
Bromobenzene (CH_3CN, $LiClO_4$), cpe 2.0 V *vs.* Ag, Ag^+ (0.01 *M*)	Pt	*p*-Dibromobenzene (trace)	551
Chlorobenzene (H_2O, H_2SO_4)	PbO_2	*p*-Chlorophenol, benzoquinone, succinic acid	208
p-Fluorotoluene (H_2O, H_2SO_4)	PbO_2	*p*-Fluorobenzoic acid (10)	243
Iodosobenzene diacetate (HOAc, H_2SO_4)	Pt	Iodoxybenzene (32)	228
o-Iodotoluene			
(a) (H_2O, H_2SO_4)	PbO_2	*o*-Iodobenzoic acid, *o*-iodobenzaldehyde	228
(b) (HOAc, H_2SO_4)	Pt	*o*-Iodosobenzoic acid (83)	228
p-Iodotoluene			
(a) (H_2O, H_2SO_4)	PbO_2	*p*-Iodobenzoic acid, *p*-iodobenzaldehyde	228
(b) (HOAc, H_2SO_4)	Pt	*p*-Iodobenzoic acid (22), *p*-iodobenzaldehyde (32)	228
(c) (CH_3CN, benzene, $LiClO_4$), cpe 1.6 V *vs.* Ag, Ag^+ (0.01 *M*)	Pt	*p*-Methyldiphenyliodonium perchlorate (44)	551
p-Iodobenzoic acid (HOAc, H_2SO_4)	Pt	*p*-Iodoxybenzoic acid	228
p-Bromotoluene (HOAc, HNO_3)	Pt	*p*-Bromobenzoic acid (good yield)	124
p-Chlorotoluene (H_2O, H_2SO_4)	Pt, PbO_2	*p*-Chlorobenzoic acid (33.6), *p*-chlorobenzaldehyde (1.4)	157, 208
2,4-Dichlorotoluene (H_2O, H_2SO_4)	PbO_2	2,4-Dichlorobenzoic acid	208

[a] Reaction product (propene) treated with Br_2. [b] No diaphragm used. [c] HOAc concn ≫ H_2SO_4 concn. [d] Major product.

ions (Eq 102–104) as exemplified by formation of rearranged N-*t*-pentylacetamide from the oxidation of neopentyl iodide (551).

$$RI \xrightarrow{-e} RI\cdot^+ \rightarrow R^+ + {}^1/_2 I_2 \qquad \text{(Eq 102)}$$

$$R^+ + CH_3CN \rightarrow RN{=}\overset{+}{C}CH_3 \qquad \text{(Eq 103)}$$



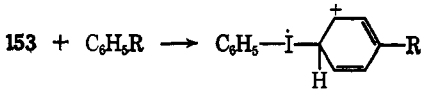
$$RN{=}\overset{+}{C}{-}CH_3 + H_2O \rightarrow CH_3\overset{\overset{\displaystyle O}{\|}}{C}HNR \qquad \text{(Eq 104)}$$

In contrast, aryl iodides do not undergo carbon–iodine bond scission but couple on electrooxidation. Thus the major product of iodobenzene oxidation in CH_3CN containing $LiClO_4$ is 4-iododiphenyliodonium perchlorate (**155**, R = I), while in the presence of excess benzene, diphenyliodonium perchlorate (**155**, R = H) results. The mechanism of the reaction is pictured as an attack of anodically generated iodobenzene cation radical **153** on an unreacted iodobenzene molecule forming the cation **154**, which decomposes to **155** by formal loss of a proton and an electron (Eq 105–107). The trapping of intermediates by benzene, which has been established to be electroinactive in the potential region of the electrolysis, demonstrates the reactivity of iodoaryl cation radicals toward aromatic molecules and suggests that **154** does not arise by cation radical dimerization.

The cation radical **153** is a likely intermediate in the formation of a number of products including iodosobenzene diacetate and iodobenzene difluoride derived from the electrolysis of iodobenzene in solutions containing acetic acid or silver fluoride, respectively.

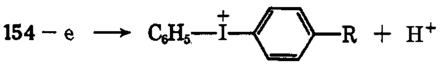
$$C_6H_5I - e \longrightarrow C_6H_5I\cdot^+ \qquad \text{(Eq 105)}$$

153



(Eq 106)

154



(Eq 107)

155

A number of aromatic halides, which are not oxidized at the halide but rather the side-chain site, have been tabulated for purposes of comparison. Several examples indicate that at Pt, oxidation of both the halide and side chain can occur, while at PbO_2 as the anode, only the side chain is attacked.

H. OXIDATION OF ORGANOMETALLIC COMPOUNDS (TABLE XV)

Electrolysis of Grignard solutions constitutes an alternative method to the Kolbe reaction for preparation of dimers. The nature of the products is consistent with formation of organic radicals at the anode since substances are also produced which derive from hydrogen abstraction from the solvent and from disproportionation to olefin and alkene. However, unlike the Kolbe electrosynthesis in which the oxidation of salts of aromatic carboxylic acids gives the coupling product with difficulty (259, 779a, 822), electrolysis of aromatic Grignard reagents represents a successful method for obtaining biphenyls.

The pioneering work of Evans and others on the behavior of the Grignard reagent during electrolysis showed that magnesium was deposited at the cathode while alkyl radicals were generated at the anode (193–197). At attackable anodes new organometallics were formed. Evans proposed the following reaction scheme.

$$\text{anodic reaction}\begin{cases} RMgX_2^- \rightarrow R\cdot + MgX_2 + e & \text{(Eq 108)} \\ R_2MgX^- \rightarrow R\cdot + RMgX + e & \text{(Eq 109)} \\ R_3Mg^- \rightarrow R\cdot + R_2Mg + e & \text{(Eq 110)} \end{cases}$$

$$\text{cathodic reaction} \quad 2MgX^+ + 2e \rightarrow 2MgX \rightarrow Mg + MgX_2 \quad \text{(Eq 111)}$$

A recent polarographic study remains in general agreement with the proposal (646, 647). Bis(organomagnesium) compounds are readily oxidized at the dropping mercury electrode in a two-electron process to give the dialkylmercury (Eq 112). Grignard reagents and the corresponding $R_2Mg + MgBr_2$ mixture are polarographically indistinguishable. Data supporting the existence of a Schlenk equilibrium (Eq 113) in these systems are presented.

$$R_2Mg + Hg \rightarrow R_2Hg + Mg^{2+} + 2e \quad \text{(Eq 112)}$$

$$2RMgBr \rightleftharpoons R_2Mg + MgBr_2 \quad \text{(Eq 113)}$$

The electrooxidation of tetraphenylborate ion (**156**) in CH_3CN at Pt is a two-electron process resulting in diphenylborinic acid (**157**) and biphenyl (Eq 114 and 115). Biphenyl is believed to be formed in an intramolecular dimerization reaction since mass spectral examination of the product produced from electrolysis of a mixture of **156** and perdeuteriotetraphenylborate ion demonstrated the presence of a mixture of biphenyls containing either all hydrogen or all deuterium (307, 309). Chemical oxidation of **156** by ceric ammonium nitrate in CH_3CN proceeds analogously.

$$\underset{\mathbf{156}}{B(C_6H_5)_4^-} \rightarrow B(C_6H_5)_2^+ + (C_6H_5)_2 + 2e \quad \text{(Eq 114)}$$

$$B(C_6H_5)_2^+ + H_2O \rightarrow \underset{\mathbf{157}}{B(C_6H_5)_2OH} + H^+ \quad \text{(Eq 115)}$$

$$\mathbf{157} + 2H_2O \rightarrow B(OH)_3 + (C_6H_5)_2 + 2H^+ + 2e \quad \text{(Eq 116)}$$

In aqueous solution at graphite, oxidation of **156** occurs in three discrete steps (789). First, **156** undergoes an irreversible two-electron transfer (cpe) to produce the diphenylborinium ion and biphenyl (Eq 114), followed by chemical reaction of diphenylborinium ion with water to give diphenylborinic acid (**157**) and hydrogen ion (Eq 115). At a higher potential, **157** may be further oxidized in a two-electron process to biphenyl, boric acid, and hydrogen ions (Eq 116).

Electrolysis of tetraalkylborates in aqueous solution at anodes capable of forming stable metal alkyls, such as Pb, Bi, Hg, Sb, Sn, or Mg, has been reported to be a good method of preparation of organometallic compounds (886, 888).

At attackable anodes, electrolysis of the molten complex $NaF\cdot 2Al(C_2H_5)_3$ is an excellent method of producing metal alkyls of Pb, Sb, Sn, Mg, Zn, and In. An equivalent amount of Al is deposited at the cathode which may be reconverted into triethylaluminum with hydrogen and ethylene in the over-all process

$$M + {}^1/_2H_2 + C_2H_4 \rightarrow M(C_2H_5) \quad \text{(Eq 117)}$$

Similar results are obtained with other organoaluminum derivatives (875, 879).

Electrolysis of cyclopentadienylmetal compounds of Na, K, Li, Tl, Fe, and Cu at a manganese anode results in formation of the cyclopentadienylmanganese, or, in presence of CO or $Fe(CO)_5$, the corresponding cyclopentadienylmanganese tricarbonyl (314).

I. ELECTROLYSIS (NON-KOLBE) OF CARBOXYLIC ACIDS

Beyond a brief definition, the Kolbe reaction will not be considered (see Introduction), but rather the various "side reactions" frequently observed in the electrolysis of carboxylic acids. The subject has been reviewed by Eberson (161) who has adequately dealt with the experimental and mechanistic aspects associated with these reactions. To avoid unnecessary duplication of effort, tables of examples and a few brief notes are presented here. The reader is referred to the bibliography and Eberson's critical account for further details.

Table XVI is arranged in the following sequence: (a) electrolysis of carboxylic acids resulting in increased unsaturation, (b) alkylation and arylation, (c) hydroxylation, (d) alkoxylation, (e) introduction of nitrogen functions, (f) acyloxylation, (g) rearrangement, esterification, and halogenation. The tabulation of examples is somewhat arbitrary since the majority of carboxylic acids exhibit reactions characteristic of several of the above classifications.

The Kolbe electrosynthesis occurs by discharge of the carboxylate anion followed by decarboxylation and dimerization of the resultant radicals (Eq 118–120). The dimerization process is successful with those radi-

TABLE XV

OXIDATION OF ORGANOMETALLIC COMPOUNDS

Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
Methyl magnesium halide			
(a) (Ether)	Pt	C_2H_6, CH_4, C_2H_4, CO_2	195–197
(b) (Pyridine)	Pt	Solid containing magnesium, gas	781
Ethyl magnesium halide			
(a) (Ether)	Pt	C_2H_6, C_2H_4	197
(b) (Ether)[a]	Pb	Tetraethyllead	67, 68, 313, 580
n-Propylmagnesium bromide (ether)	Pt	Propane, propene, hexane, propyl alcohol, *sec*-amyl alcohol, C_2H_4, C_2H_5OH, CO_2	193
Isopropylmagnesium bromide (ether)	Pt	Propane, propene, 2,3-dimethylbutane, C_2H_4, CO_2, C_2H_5OH, isopropyl alcohol	193, 194, 197
n-Butylmagnesium bromide (ether)[b]	Hg	Octane (85), butene-1, butane	193, 568
Isobutylmagnesium bromide (ether)	Pt	2,5-Dimethylhexane (96)	194
sec-Butylmagnesium bromide (ether)	Pt	3,4-Dimethylhexane (49)	194
t-Butylmagnesium bromide (ether)	Pt	Tetramethylbutane	194
n-Amylmagnesium bromide (ether)[b]	Hg	Decane (55–60)	568
Isoamylmagnesium chloride (ether)	Al, Bi, Au, Ni, Ag, Sn, Zn, Cd	Metal alkyl (for Al, Zn, Cd)	288, 609
n-Hexylmagnesium bromide (ether)[b]	Hg	Dodecane (45)	194, 568
n-Heptylmagnesium bromide (ether)[b]	Hg	Tetradecane (50)	568
n-Octylmagnesium bromide (ether)[b]	Hg	Hexadecane (47)	568
n-Nonylmagnesium bromide (ether)[b]	Hg	Octadecane (55–60)	568
n-Decylmagnesium bromide (ether)[b]	Hg	Eicosane (35)	568
n-Undecylmagnesium bromide (ether)[b]	Hg	Docosane (5–6)	568
n-Dodecylmagnesium bromide (ether)[b]	Hg	Tetracosane (40)	568
n-Tetradecylmagnesium bromide (ether)[b]	Hg	Octacosane (40)	568
n-Hexadecylmagnesium bromide (ether)[b]	Hg	Dotriacontane (52)	568
n-Octadecylmagnesium bromide (ether)[b]	Hg	Hexatriacontane (54)	568
Cyclopentylmagnesium bromide (ether)[b]	Hg	Dicyclopentyl (35)	568
Cyclohexylmagnesium bromide (ether)[b]	Hg	Dicyclohexyl (53)	567
Pinenemagnesium chloride (ether)[b]	Hg	Dibornyl (20)	567
Geranylmagnesium bromide (ether)[b]	Hg	Digeranyl (60)	568
Fenchylmagnesium bromide (ether)[b]	Hg	Difenchyl (35)	568
Menthylmagnesium bromide (ether)[b]	Hg	Dimenthyl (48–50)	567, 568
Phenylmagnesium bromide (ether)	Hg	Biphenyl (55)	567
α-Naphthylmagnesium bromide (ether)[b]	Hg	1,1′-Binaphthyl (43)	567
Bis(indenyl)magnesium (dimethyl ether, indene)	Mn	Bis(indenyl)manganese (good)	314
Phenyllithium (ether)	Hg	Biphenyl (50–60)	567
Ethylsodium, ethylzinc, triethylaluminum	Pb, Bi	Propane, butane, C_2H_6, C_2H_4, metal alkyl	343–345
Sodium acetylide (liq NH_3)	. . .	Acetylenes, olefins	723, 724
Methylcyclopentadienylsodium			
(a) (Diglyme, tetrahydrofuran)	Mn	Manganese bis(methylcyclopentadienide)	314
(b) (Diglyme, CO)	Mn	Methylcyclopentadienylmanganese tricarbonyl (good)	314
n-Decylcyclopentadienylsodium and -potassium (diethylene glycol dibutyl ether)	Mn	*n*-Decylcyclopentadienylmanganese	314
Ethylzinc (ether)	Pt	Unidentified	672
Diphenylzinc (ether)	Hg	Biphenyl (60)	567
Diphenylcadmium (ether)	Hg	Biphenyl (60)	567
Cyclopentadienylthallium (DMF, $LiClO_4$)	Hg	Dicyclopentadienylmercury	303
Bis(1,2-diethylcyclopentadienyl)thallium (butyrolactone, $Ni(CO)_4$)	Mn	1,2-Diethylcyclopentadienylmanganese tricarbonyl (good)	314
Lead diacetate (HOAc, KOAc)	Pt	Lead tetraacetate (quant)	277
Sodium triphenylgermanium (liq NH_3)	Pt, Hg	Hexaphenyldigermane (10–35), triphenylgermane (90–65)	286
n-Butylboronic acid (H_2O, base)	Pt	Boric acid, *n*-butane (trace), butene-1, *cis*-butene-2, *trans*-butene-2[c]	363
Benzeneboronic acid (H_2O, base)	Pt	Recovered sm	363
Tetramethylammonium tetraphenylborate (CH_3CN, $NaClO_4$), cpe 1.0 V *vs.* sce	Pt	Biphenyl, diphenylborinium perchlorate	309
Sodium tetraphenylborate			
(a) (H_2O, pH 4.6), cpe 0.5 V *vs.* sce	C	Biphenyl, diphenylborinic acid[d]	789
(b) (H_2O, pH 4.6), cpe 1.1 V *vs.* sce	C	Biphenyl, boric acid	789
Sodium tetraethylborate (H_2O)	(a) Pb	Tetraethyllead (91), triethylboron (95.5), C_2H_6, C_2H_4, C_4H_{10}	886, 888
	(b) Bi	Triethylbismuth (98), triethylboron (94)	886, 888
	(c) Hg	Diethylmercury (81), triethylboron (87)	886, 888
	(d) Sb	Triethylantimony (82)	886, 888
	(e) Sn	Tetraethyltin (10)	886, 888
	(f) Mg	Diethylmagnesium (73), triethylboron (97)	886

TABLE XV (*Continued*)

Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
Sodium tetramethylborate (H_2O)	Pb	Tetramethyllead (78), trimethylboron	888
$NaB(C_3H_7)_4 + Na(C_3H_7)_3BOCH_3$ (tetrahydrofuran)	Pb	Tetrapropyllead, tripropylboron	886
Triethylaluminum	Pb	Tetraethyllead	191, 874, 876, 880
$NaAl(CH_3)_4 + NaAl(C_2H_5)_4$	(a) Pb[f]	Tetraethyllead (77)	432
	(b) Sn[g]	Tetraethyltin[h]	431
	(c) Mg[i]	Dimethylmagnesium, methylethylmagnesium, diethylmagnesium	430
	(d) Zn[k]	Diethylzinc	429
$Na[Al(C_2H_5)_3(OC_4H_9)]$	(a) Pb	Tetraethyllead (93)	877, 882, 884, 887
	(b) Zn	Diethylzinc (91)	882, 884
	(c) Sn	Tetraethyltin (85)	882, 884
	(d) Sb	Triethylantimony (96)	882, 884
	(e) Bi	Triethylbismuth (95)	882, 884
	(f) Cd	Diethylcadmium (81)	882, 884
	(g) Hg	Diethylmercury (82)	882, 884
$NaF \cdot 2Al(C_2H_5)_3$[j]	(a) Pb	Tetraethyllead (quant)	880, 881, 885
	(b) Sb	Triethylantimony (90)	881
	(c) Sn	Tetraethyltin	881
	(d) Mg	Diethylmagnesium	881
	(e) Zn	Diethylzinc	881
	(f) In	Triethylindium	881
$NaAl(C_2H_5)_4 + KAl(C_2H_5)_4 + KCl$	Pb	Tetraethyllead (92)	883
$NaAl(C_3H_7)_4 + KAl(C_3H_7)_4 + KCl$	Zn	Dipropylzinc (88)	883
$NaAl(CH_3)_4$ (tetrahydrofuran)	Pb	Tetramethyllead (90)	878
Tris(fluorenyl)aluminum (diethyl ether)	Mn	Bis(fluorenyl)manganese (good)	314
Ferrocene (H_2O, $HClO_4$, $LiClO_4$)	C paste[e]	Ferrocene cation	460
Bis(butyl)cyclopentadienyliron (DMF, CO)	Fe–Mn	Butylcyclopentadienylmanganese tricarbonyl (good)	314
Copper phenylcyclopentadienide (benzene, $Al(C_2H_5)_3$, $Fe(CO)_5$)	Mn	Phenylcyclopentadienylmanganese tricarbonyl (good)	314

[a] Diethyl ether, tetrahydrofuran, ethylene glycol dimethyl ether, diethylene glycol dibutyl ether, or diisopropyl ether. [b] Reaction also carried out with corresponding Li, Cd, and Zn alkyls. [c] Olefins in proportion 3.3:1:1, respectively. [d] Film deposited on anode. [e] Voltammetric study. [f] Similarly prepared: $Pb(i\text{-}C_3H_7)_4$, $Pb(C_6H_5)_4$, $Pb(C_{10}H_{21})_4$, and $Pb(CH_3)_4$. [g] Similarly prepared: $Sn(i\text{-}C_3H_7)_4$, $Sn(C_6H_5)_4$, $Sn(C_8H_{17})_4$, and $Sn(CH_3)_4$. [h] Major product. [i] Similarly prepared: $Mg(C_3H_7)_2$, $Mg(C_6H_5)_2$, and $Mg(C_4H_9)_2$. [j] Mp 35°. [k] Similarly prepared: $Zn(C_3H_7)_2$, $Zn(C_6H_5)_2$, $Zn(C_{10}H_{21})_2$, and $Zn(CH_3)_2$.

cals which are resistant to further oxidation. These have ionization potentials greater than about 8 eV (methyl 9.95, ethyl 8.75, isobutyl 8.35, cyanomethyl 10.87, dimethylcyanomethyl 9.15 eV). Radicals having ionization potentials less than 8 eV undergo oxidation to carbonium ions (Eq 121). In this group are secondary and tertiary radicals (isopropyl 7.90, *t*-butyl 7.42), alicyclic radicals (cyclobutyl 7.88, cyclopentyl 7.80, cyclohexyl 7.60), benzyl 7.76, and benzhydryl 7.32 eV (163). Thus depending on the structure of the carboxylic acid, radical processes (dimerization, initiation of polymerization, disproportionation, hydrogen abstraction, etc.) or carbonium ion processes (reaction with nucleophiles, rearrangement, deprotonation, etc.) are likely to occur.

Other factors, however, are also of great importance in determining the outcome of the reaction. Formation of the Kolbe product is favored at a smooth platinum anode, high current density, and with CH_3OH or DMF as solvent, while carbonium ion pathways are enhanced at a carbon anode, in alkaline solution, with increased temperature, and with added ions such as ClO_4^-, SO_4^{2-}, HCO_3^-, $H_2PO_4^-$, and F^-. Anodically generated carbonium ions are believed to be of the "hot" variety since the products resemble those of hot carbonium ion reactions in homogeneous solution (302, 433, 785).

$$RCO_2^- \rightarrow RCO_2\cdot + e \qquad \text{(Eq 118)}$$

$$RCO_2\cdot \rightarrow R\cdot + CO_2 \qquad \text{(Eq 119)}$$

$$2R\cdot \rightarrow R{-}R \qquad \text{(Eq 120)}$$

$$R\cdot \rightarrow R^+ + e \qquad \text{(Eq 121)}$$

J. MISCELLANEOUS OXIDATIONS (TABLE XVII)

The oxidation of simple alkyl-substituted hydrazines has been examined recently (418, 450). Methylhydrazine undergoes an over-all four-electron reaction to nitrogen and CH_3OH in acid solution according to Eq 122. Oxidation of 1,2-dimethylhydrazine proceeds by an initial two-electron oxidation, followed by a chemical reaction which results in formaldehyde and methylhydrazine. Coulometric results indicate that six electrons are involved in total. The reaction mechanism (Eq 123–126) is similar to that proposed for chemical oxidation of 1,2-dimethylhydrazine with iodate (526).

$$CH_3NHNH_3^+ + H_2O \rightarrow CH_3OH + N_2 + 5H^+ + 4e \qquad \text{(Eq 122)}$$

TABLE XVI

ELECTROLYSIS (NON-KOLBE) OF CARBOXYLIC ACIDS

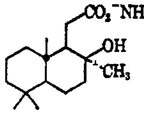
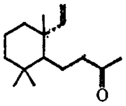
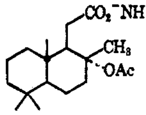
Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
		(a) Electrolysis of Carboxylic Acids Resulting in Increased Unsaturation	
Acetic acid (H_2O, KOH)	C	C_2H_6 (6.4), methyl acetate (82)	433
t-Alkylmalonic half-esters (CH_3OH, $NaOCH_3$)	Pt	2,3-Di(*t*-alkyl)succinates, monomers consisting of olefins, alkoxylation and ester products	170
Butyric acid (H_2O, KOH)	C	Propylene (a) and cyclopropane (b) (a:b = 2:1), isopropyl butyrate, *n*-propyl butyrate	433
Isobutyric acid (H_2O, KOH)	C	Propylene (60), isopropyl isobutyrate (2)	433
2- or 3-Methylbutyric acid (H_2O, KOH)	C	Isobutane, 1-butene, isobutylene, *cis*-2-butene, methylcyclopropane	433
Valeric acid (H_2O, KOH)	C	1-Butene, *n*-butane, isobutylene, *trans*-2-butene, *cis*-2-butene, methylcyclopropane, 2-butanol, *t*-butyl alcohol, 1-butanol, 2,5-dimethylhexane, esters	433
Fumaric acid, maleic acid, or acrylic acid (aqueous solution)	Pt	Acetylene, CO_2	218, 237, 409, 630
Itaconic acid (aqueous solution)	Pt	Allene, acrylic acid, mesaconic acid, CO_2	1, 502
Potassium glutarate (H_2O)	...	Propylene, CO_2	801
Sodium *β*,*β*-dimethylglutarate	Pt	2-Methylbutene (2 g/200 g of acid)	817
Hex-3-enoic acid (H_2O, KOH)	Pt	1,2-Pentadiene, hex-3-enyl hex-3-enoate	222, 822
Adipic acid	...	Butene-2, butene-1, CO_2	802
Potassium cyclopropanecarboxylate (H_2O)	Pt	Allyl cyclopropanecarboxylate, CO_2	238
Sodium 1,2-*cis*-cyclopropanedicarboxylate (H_2O)	Pt	Allene, CO_2	253
cis-1,2-Cyclobutanedicarboxylic acid (CH_3OH)	Pt	Cyclobutene (5)	616
Medium-ring cycloalkanecarboxylic acids (H_2O, NaOH)	C	*cis*- and *trans*-Cycloalkenes, bicyclo[*x*.1.0] and -[*y*.3.0]-alkanes, alcohols, esters	785
 (CH_3OH)	Pt	 (34–38) Kolbe dimer (12)	133
 (CH_3OH)	Pt	Kolbe dimer (34)	133, 134
trans-1,2-Dihydrophthalic acid	Pt	Benzene (70)	613
Benzoic acid (CH_3OH, sodium benzoate)	Pt	Benzene (0.066 g/faraday)	234
4-*t*-Butyl-2,6-dimethylbenzoic acid (CH_3OH, sodium salt of acid)	Pt	Dimethyl 2-methyl-4-*t*-butylphthalate (10–20), 1,3-dimethyl-5-*t*-butylbenzene (30–40)	234, 260
3-Phenylisovaleric acid (CH_3OH, NaOAc)	Pt	*t*-Amylbenzene (32), 2,5-diphenyl-2,5-dimethylhexane, *α*,*β*-dimethylstyrene	72, 798
meso- or *dl*-2,3-Diphenylsuccinic acid (H_2O, $(C_2H_5)_3N$)	Pt	*trans*-Stilbene (40–50) (no *cis*)	132
		(b) Alkylation and Arylation	
Vinyl acetate (H_2O, KOAc)	Pt	Polyvinyl acetate (38 g/100 gsm)	730
Vinyl chloride (H_2O, KOAc)	Pt	Polymer (0.65 g/120 mlsm)	730
Methyl methacrylate (H_2O, KOAc)	Pt	Poly(methyl methacrylate) (15.5 g/100 gsm)	73, 294, 730
Styrene			
(a) (HOAc, NaOAc)^a	Pt	*meso*-3,4-Diphenylhexane (0.5 g/20 gsm), polymer (mol wt 3200; 0.09 g)	73, 318
(b) (HOAc, NaOAc)^b	Pt	*meso*-3,4-Diphenylhexane (5.1 g/87.5 gsm), *α*-methylphenethyl acetate, polymer (4.3 g)	318
(c) ($CH_3CH_2CO_2H$, $CH_3CH_2CO_2K$)	Pt	*meso*-4,5-Diphenyloctane (0.26 g/12 gsm), polymer (0.07 g)	318
Acrylonitrile (HOAc, NaOAc)	Pt	Polyacrylonitrile	73, 318
Cyclohexene (CH_3OH, disodium malonate)	...	Norcarane (nil), cyclohex-2-enyl methyl ether	738
Vinylpyrrolidone (CH_3OH, KOAc)	Pt	Polyvinylpyrrolidone	293
Perfluoroethylene (CF_3CO_2H, $(CF_3CO)_2O$, CF_3CO_2K)	Pt	Perfluoro polymer	316
Chlorotrifluoroethylene (CF_3CO_2H, $(CF_3CO)_2O$, CF_3CO_2K)	Pt	Perhalo polymer	316
Fluorotrichloroethylene (CF_3CO_2H, $(CF_3CO)_2O$, CF_3CO_2K)	Pt	$CCl_3(C_2FCl_3)_{10}CCl_3$ (30 g/50 gsm)	316
Butadiene			
(a) (CH_3OH, HOAc, KOAc)	Pt	C_{10} dienes (12–58), 3-hexene (11–26)	488
(b) (CH_3OH, HOAc, KOAc)	Pt	*trans*-3-Hexene (56), 1-pentene (22), 3-methyl-1-pentene (16), methyl acetate, CH_3OH, C_{10} hydrocarbons, C_5 acetate esters	729
(c) (CH_3OH, CF_3CO_2H, CF_3CO_2K)	Pt	1,1,1,10,10,10-Hexafluoro-3,7-decadiene	488
(d) (CH_3OH, $CH_3CH_2CO_2H$, $CH_3CH_2CO_2K$)	Pt	*trans*-4-Octene, esters	731

TABLE XVI (*Continued*)

Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
(e) (CH_3OH, ethyl hydrogen oxalate, potassium salt)	Pt	Diethyl 3,7-decadiene-1,10-dioate	488, 489
(f) (CH_3OH, oxalic acid, KOH)	Pt	2,6-Octadiene-1,8-dicarboxylic acid, dimethyl 2,6-octadiene-1,8-dicarboxylate (total yield 40%)	276
(g) (CH_3OH, ethyl hydrogen maleate, potassium salt)	Pt	Diethyl 2,5,8-decatriene-1,10-dioate	488
(h) (CH_3OH, sodium (+)-α-methylbutyrate)	Pt	3,12-Dimethyl-5,9-tetradecadiene (inactive), butane, esters, 1-butene, *trans*-2-butene, *cis*-2-butene^c	731
(i) (CH_3OH, methyl hydrogen adipate, KOH)	Pt	Dimethyl 6,10-hexadecadiene-1,6-dicarboxylate (67), dimethyl 6-dodecene-1,12-dicarboxylic acid (22.3), dimethyl sebacate (8.5), dimethyl adipate	274, 275, 278
Isoprene			
(a) (CH_3OH, HOAc, KOAc)	Pt	3-Methyl-3-hexene	488
(b) (CH_3OH, HOAc, KOAc)	Pt	*cis*-3-Methyl-3-hexene,^{d} methyl acetate, C_{12} hydrocarbons, acetate esters	729
1,3-Cyclohexadiene (CH_3OH, HOAc, KOAc)	Pt	*trans*-1,4-Dimethylcyclohexane (14),^{e} *trans*-1,2-dimethylcyclohexane (27), *cis*-1,2-dimethylcyclohexane (15), cyclohexane (2), methylcyclohexane, methoxylated cyclohexanes	731
cis- or *trans*-Methyl hydrogen hexahydrophthalate (CH_3OH, $NaOCH_3$)	Pt	Methyl 1-cyclohexene-1-carboxylate + methyl 2-cyclohexene-1-carboxylate + methyl cyclohexanecarboxylate (47), *trans, anti, trans*- and *trans, syn, trans*-perhydrodiphenic acid dimethyl esters (32)	251, 607
trans, anti, trans- or *trans, syn, trans*-Perhydrodiphenic acid (CH_3OH, $NaOCH_3$)	Pt	*trans*-2-(1-Hydroxycyclohexyl)cyclohexanecarboxylic acid lactone (45)	608
cis, syn, cis-Perhydrodiphenic acid (CH_3OH, $NaOCH_3$)	Pt	*cis*-2-(1-Hydroxycyclohexyl)cyclohexanecarboxylic acid lactone (40)	608
trans, trans, trans-1,3-Dicarboxy-2,4-dicarbomethoxycyclobutane (CH_3OH, $NaOCH_3$)	Pt	2,4-Dicarbomethoxybicyclobutane (0.1 g/1 gsm)	806
Nitrobenzene (HOAc, KOAc)	Pt	*o*-Nitrotoluene and other methylated aromatics	338
Trinitrotoluene (HOAc, KOAc)	Pt	Trinitro-*m*-xylene (9)	269
Pyridine			
(a) (H_2O, NaOH, benzoic acid)	Pt	2-, 3-, and 4-Phenylpyridines (distribution 56:35:9), biphenyl-4-carboxylic acid, 2-pyridone, biphenyl (nil), polymer	83, 256
(b) (Diethylammonium benzoate)	Pt	Biphenyl, 4-phenylpyridine, biphenyl-4-carboxylic acid	259
o-Benzoylbenzoic acid (CH_3OH, C_5H_5N, $NaOCH_3$)	Pt	Fluorenone and fluoren-9-ol (10), benzophenone	84
o-(*p*-Chlorobenzoyl)benzoic acid (CH_3OH, C_5H_5N, $NaOCH_3$)	Pt	3-Chlorofluorenone and 3-chlorofluoren-9-ol (10), *p*-chlorobenzophenone	84
		(c) Hydroxylation	
Acetic acid (NaOAc)	Pt	CH_3OH (93), CO_2, HCHO, C_2H_6	206, 356, 455–457
4,4,4-Trinitrobutanoic acid (H_2O, $KHCO_3$)	. . .	3,3-Dinitro-2-hydroxypropionic acid (23.8), CO_2	453
Potassium cyclobutanecarboxylate (H_2O)	Pt	Cyclobutanol, CO_2, cyclobutyl cyclobutanecarboxylate	145
Cyclobutanecarboxylic acid (H_2O, $(C_2H_5)_3N$)	Pt	Cyclobutanol, cyclopropylcarbinol, allylcarbinol, CO_2	131
4-Methylcyclohexanecarboxylic acid (H_2O, $KHCO_3$)	Pt	4-Methylcyclohexanol, 4-methylcyclohexanone, 4-methylcyclohex-1-ene, Kolbe dimer, CO_2, 4-methylcyclohexanecarboxylic acid 4-methylcyclohexyl ester	250
cis- and *trans*-Bicyclo[3.1.0]hexane-3-carboxylic acids (H_2O, C_5H_5N)	Pt	*cis*- and *trans*-Bicyclo[3.1.0]hexan-2-ols, ketones	302
1-Methylcyclohexaneacetic acid (H_2O, base or acid)	Pt	1-Methylcyclohexanecarboxaldehyde (13–21), 1-methylcycloheptanol (49–59), 1,2-di(1-methylcyclohexyl)-ethane (8), CO_2	575
Leucinic acid (H_2O, H_2SO_4)	PbO_2	Isovaleric acid (30), isoamyl alcohol (10), isovalerylleucinecarboxylic acid (3), isovaleric acid isoamyl ester (5), CO_2	758
Phenylacetic acid	. . .	Benzyl alcohol, CO_2, benzaldehyde	629
Potassium diphenylacetate	Pt	Diphenylcarbinol, CO_2, diphenylmethyl diphenylacetate	401
o-Nitrobenzoic acid (Ac_2O, potassium salt)	Pt	*o*-Nitrophenol, CO_2, nitrobenzene, *o*-nitrophenyl *o*-nitrobenzoate	696
Pyrrolidonecarboxylic acid (H_2O, H_2SO_4)	PbO_2	Succinimide (3.2 g/6.5 gsm), succinic acid, CO_2	756
		(d) Alkoxylation	
Diphenylacetic acid (CH_3OH, C_5H_5N, or $(C_2H_5)_3N$)	Pt	Diphenylmethyl methyl ether (35–80)	272, 354, 800
Triphenylacetic acid (CH_3OH, $NaOCH_3$)	Pt	Triphenylmethyl methyl ether (60)	493
α-Methoxyphenylacetic acid (CH_3OH, $NaOCH_3$)	Pt	Benzaldehyde dimethyl acetal (61.6)	842
α-Ethoxyphenylacetic acid (CH_3OH, $NaOCH_3$)	Pt	Benzaldehyde methyl ethyl acetal (71.4)	842
4-Methoxyphenylacetic acid (CH_3OH, $NaOCH_3$)	Pt	4-Methoxyphenylmethyl ether (64), 4-methoxybenzaldehyde dimethyl acetal (24)	846
4-Nitrophenylacetic acid (CH_3OH, $NaOCH_3$)	Pt	4-Nitrophenylbenzyl methyl ether (16), 4-nitrophenylbenzyl alcohol (7), 4-nitrophenylbenzaldehyde (trace), 1,2-bis(*p*-nitrophenyl)ethane (32.6)	843

TABLE XVI (*Continued*)

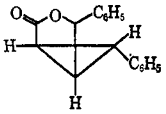
Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
3-Nitrophenylacetic acid (CH_3OH, $NaOCH_3$)	Pt	3-Nitrobenzaldehyde (7.9)	843
2-Nitrophenylacetic acid (CH_3OH, $NaOCH_3$)	Pt	2-Nitrophenylbenzyl methyl ether (16.7), 2-nitrophenylbenzyl alcohol (trace), 2-nitrophenylbenzaldehyde (trace)	843
4,4'-Dinitrodiphenylacetic acid (CH_3OH, $NaOCH_3$)	Pt	4,4'-Dinitrodiphenylmethyl methyl ether (63)	843
2,4-Dinitrophenylacetic acid (CH_3OH, $NaOCH_3$)	Pt	2,4-Dinitrobenzaldehyde (21), 2,4-dinitrobenzyl alcohol (trace)	843
α-Methoxyphenylacetic acid (C_2H_5OH, $NaOC_2H_5$)	Pt	Benzaldehyde methyl ethyl acetal (50)	845
α-Ethoxyphenylacetic acid (C_2H_5OH, $NaOC_2H_5$)	Pt	Benzaldehyde diethyl acetal (73)	845
4-Nitro-α-ethoxyphenylacetic acid (CH_3OH, $NaOCH_3$)	Pt	4-Nitrobenzaldehyde methyl ethyl acetal (50)	844
α-Methoxydiphenylacetic acid (CH_3OH, $NaOCH_3$)	Pt	Benzophenone dimethyl acetal (74)	842
α-Ethoxydiphenylacetic acid (CH_3OH, $NaOCH_3$)	Pt	Benzophenone methyl ethyl acetal (74)	842
4,4'-Dimethoxydiphenylacetic acid (CH_3OH, $NaOCH_3$)	Pt	4,4'-Dimethoxydiphenylmethyl methyl ether (65), 4,4'-dimethoxybenzophenone dimethyl acetal (14)	846
α-Ethoxydiphenylacetic acid (C_2H_5OH, $NaOC_2H_5$)	Pt	Benzophenone diethyl acetal (77)	845
t-Butylacetic acid (CH_3OH)	Pt	*t*-Amyl methyl ether (9), 2-methylbutene-1 (5), neopentyl *t*-butyl acetate (5), 2,2,5,5-tetramethylhexane (65)	575
Potassium laurate			
(a) (CH_3OH, KCl)	C	1-Hendecene (18), 1-methoxyhendecane (55), methyl laurate (17)	452
(b) (Ethylene glycol, KCl)	C	2-Hendecyloxyethanol (34), lauric acid (51)	452
N-Benzoylglycine (CH_3OH, $NaOCH_3$)	Pt	N-Methoxymethylbenzamide (61)	495
N-Acetylglycine (CH_3OH, $NaOCH_3$)	Pt	N-Methoxymethylacetamide (78)	495
N-Carbobenzyloxyglycine (CH_3OH, $NaOCH_3$)	Pt	Benzyl-N-methoxymethylurethan (74), 1,2-biscarbobenzyloxyaminoethane	495
N-Acetyl-DL-α-alanine (CH_3OH, $NaOCH_3$)	Pt	N-1'-Methoxyethylacetamide (85)	495
N-Benzoyl-DL-α-alanine (CH_3OH, $NaOCH_3$)	Pt	N-1'-Methoxyethylbenzamide (91)	495
N-Benzoylglycine (C_2H_5OH, $NaOC_2H_5$)	Pt	N-Ethoxymethylbenzamide (56), 1,2-bisbenzamidoethane	495
N-Benzoylglycine (isopropyl alcohol, ammonium salt of acid)	Pt	N-Isopropoxymethylbenzamide (70), 1,2-bisbenzamidoethane	495
N-Benzoyl-DL-α-alanine (C_2H_5OH, $NaOC_2H_5$)	Pt	N-1'-Ethoxyethylbenzamide (76)	495
Hydratropic acid (CH_3OH, $(C_2H_5)_3N$)	Pt	Methyl α-phenethyl ether (20), 2,3-diphenylbutane (*meso* and *dl*; 21), styrene, α-phenethyl alcohol, acetophenone	575
3,3-Diphenylpropanoic acid (CH_3OH, sodium salt)	Pt	1-Methoxy-1,2-diphenylethane (12.7), 1,1,4,4-tetraphenylbutane (13), 4-phenyl-3,4-dihydrocoumarin	62
2,3,3-Triphenylpropionic acid (CH_3OH, sodium salt)	Pt	Methyl 1,2,2-triphenylethyl ether (53)	62
3,3,3-Triphenylpropionic acid (CH_3OH, sodium salt)	Pt	Phenyl 3,3-diphenyl-3-methoxypropionate (16)	72
3,3,3-Tri-*p*-*t*-butylphenylpropionic acid (CH_3OH, sodium salt)	Pt	*p*-*t*-Butylphenyl 3,3-di-*p*-*t*-butylphenyl-3-methoxypropionate (23)	72
1-Methylcyclopentaneacetic acid (CH_3OH)	Pt	1-Methylcyclohexene (12), methyl 1-methylcyclohexyl ether (16), 1,2-di(1-methylcyclopentyl)ethane (58)	575
1-Methylcyclohexaneacetic acid			
(a) (CH_3OH, base)	Pt	1-Methylcycloheptene (11), methyl 1-methylcycloheptyl ether (13), 1,2-di(1-methylcyclohexyl)ethane (58)	575
(b) (C_2H_5OH)	Pt	Methylcycloheptane (2), 1-methylcycloheptene (14), ethyl 1-methylcycloheptyl ether (9), 1,2-di(1-methylcyclohexyl)ethane (57)	575
(c) (CH_3OH, methyl hydrogen succinate)	Pt	1,2-Di(1-methylcyclohexyl)ethane (39), 1-methylcycloheptene (11), methyl 1-methylcycloheptyl ether (13), methyl β-methoxypropionate (10), dimethyl adipate (5), methyl 1-methylcyclohexanebutyrate (19)	575
Cholesteryl-3β-carboxylic acid (CH_3OH, $(C_2H_5)_3N$)	Pt	6β-Methoxy-3,5-cyclocholestane, 6β-methoxy-Δ^4-cholestene, 4β-methoxy-Δ^6-cholestene, 1-cholesteryl methyl ether	36, 131
3-β-Acetoxybisnorallocholanic acid			
(a) (CH_3OH, $NaOCH_3$)	Pt	Δ^{20}-5α-Pregnen-3β-ol (11), 20-ξ-methoxy-5α-pregnan-3β-ol (42), $C_{22}H_{38}O_2$^{f} (14)	818
(b) (C_2H_5OH, $NaOC_2H_5$)	Pt	Δ^{20}-5α-Pregnen-3β-ol (30), 20-ξ-ethoxy-5α-pregnan-3β-ol (27)	818
β-Truxinic acid (CH_3OH)	Pt	1,4-Diphenyl-*trans,trans*-1,3-butadiene, 1,2-dimethoxy-3,4-diphenylcyclobutane, 	616

TABLE XVI (*Continued*)

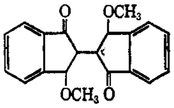
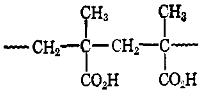
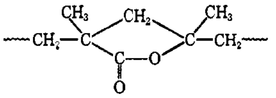
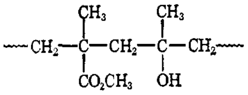
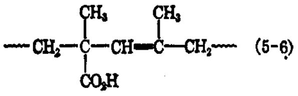
Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
Indan-2-carboxylic acid (CH_3OH, potassium salt)	Pt	Indanol-1 methyl ether, indane, 2,2′-diindanyl, indene, 	258
Dihydrosteviol A (CH_3OH, $NaOCH_3$)	Pt	4-Normethoxy-13-hydroxystevane (139 mg/671 mgsm)	819
Isostevic acid (CH_3OH, $NaOCH_3$)	Pt	4-Normethoxyisostevane (65), 4-nor-Δ^4-isostevene (25)	819
exo- or *endo*-Norbornane-2-carboxylic acid (CH_3OH, $(C_2H_5)_3N$)	Pt	*exo*-Norbornyl methyl ether (35–40), norcamphor (trace)	131
exo- or *endo*-Norbornene-2-carboxylic acid (CH_3OH, $(C_2H_5)_3N$)	Pt	3-Methoxynortricyclane (56)	131
1-Azabicyclo[2.2.2]octane-2-carboxylic acid (CH_3OH, $NaOCH_3$)	Pt	2-Methoxy-1-azabicyclo[2.2.2]octane (43)	301
Apocamphane-1-carboxylic acid (CH_3OH, base)	Pt	1,1′-Biapocamphane (33), 1-apocamphyl methyl ether (32), 1-apocamphyl apocamphane-1-carboxylate (10)	575
(e) Introduction of Nitrogen Functions			
Sodium acetate (H_2O, $NaNO_3$)	Pt	Methyl nitrate (111.5 g/1260 gsm), nitromethane (8.5 g)	230
Acetic acid (HNF_2, NaOAc), cpe 2.7–2.9 V *vs.* sce	Pt	N,N-Difluoromethylamine (68), tetrafluorohydrazine, C_2H_6	853
Perdeuterioacetic acid (HNF_2, CD_3CO_2Na) cpe	Pt	CD_3NF_2	853
Cyanoacetic acid (CH_3OH, KOH)	Pt	N-Acetylglycinonitrile (30), methyl cyanoacetate (7), succinonitrile (24)	162
Sodium propionate (H_2O, $NaNO_3$)	Pt	Ethyl nitrate, ethyl propionate, *n*-butyl nitrate, ethylene glycol dinitrate, 1,4-butanediol dinitrate	249
Propionic acid (HNF_2, sodium propionate), cpe	Pt	N,N-Difluoroethylamine	853
Sodium butyrate (H_2O, $NaNO_3$)	Pt	1-Nitropropane, *n*-hexane, isopropyl nitrate, isopropyl butyrate, 2-hexanol nitrate, 2,3-dimethyl-1-butanol nitrate, 1,2-propanediol dinitrate, 2-methyl-2,5-pentandiol dinitrate	231
Sodium adipate (H_2O, $NaNO_3$)	Pt	1,2-Butanediol dinitrate (21.5), 1,2,3-butanetriol dinitrate, 1,2,4-butanetriol dinitrate	220
Caproic acid (H_2O, NaOH, NaN_3), cpe $\geqslant 2.7$ V *vs.* sce	Pt	*n*-Decane (40), pentyl azide (48)	856
Trimethylacetic acid (H_2O, KOH, CH_3CN)	Pt	N-*t*-Butylacetamide (40)	165
t-Butylcyanoacetic acid (CH_3OH, KOH)	Pt	N-(*t*-Butylacetyl)-*t*-butylglycinonitrile (31), 1,2-di-*t*-butylsuccinonitrile (*meso*) (13), methyl *t*-butylcyanoacetate (12)	162
Potassium malonate (H_2O, KNO_3)	Pt	Glycol dinitrate, 1,4-butanediol dinitrate	255
Potassium ethyl malonate (H_2O, KNO_3)	Pt	Ethyl acetate, ethyl glycolate nitrate, diethyl succinate, ethyl glyoxalate	255
Potassium ethyl ethylmalonate (H_2O, KNO_3)	Pt	Ethyl crotonate, ethyl α-hydroxybutyrate nitrate, diethyl ethylmalonate, diethyl 1,2-diethylsuccinate	255
Potassium ethyl dimethylmalonate (H_2O, KNO_3)	Pt	Ethyl β-hydroxyisobutyrate nitrate, diethyl tetramethylsuccinic acid, ethyl methacrylate, diethyl dimethylmalonate	255
Potassium succinate (H_2O, KNO_3)	Pt	Ethylene glycol dinitrate, 1,4-butanediol dinitrate	208a
Potassium ethyl succinate (H_2O, KNO_3)	Pt	Ethyl β-hydroxypropionate nitrate, diethyl adipate, ethyl acrylate, diethyl succinate, $C_{15}H_{26}O_6$ (ester)	255
Methyl hydrogen tetramethyl succinate (H_2O, KOH, CH_3CN)	Pt	N-Acetyl-2,2,3,3-tetramethyl-β-alanine (25)	165
Potassium glutarate (H_2O, KNO_3)	Pt	1,2-Propanediol dinitrate, 1,3-propanediol dinitrate, 1,3-glycerol dinitrate	208a
Sodium cyclohexancarboxylate (H_2O, $NaNO_3$)	Pt	Cyclohexene, cyclohexanol, cyclohexanone, dicyclohexyl ether, cyclohexanol nitrate, dicyclohexyl, cyclohexyl cyclohexanecarboxylate, 1,2-cyclohexanediol dinitrate	236
		(f) Acyloxylation	
Phenylacetic acid (HOAc, NaOAc)	Pt	Benzyl acetate (40)	494
Diphenylacetic acid (HOAc, NaOAc)	Pt	Diphenylmethyl acetate (40)	494
Triphenylacetic acid (HOAc, NaOAc)	Pt	Triphenylcarbinol (50)^g	494, 726
N-Phenylacetylglycine (HOAc, NaOAc)	Pt	N-(Acetoxymethyl)phenylacetamide (38)	495
3,3-Diphenylpropanoic acid		See section III.A. 3	
Polymethacrylic acid (CH_3OH, $NaOCH_3$)  $-CH_2-\overset{CH_3}{\underset{CO_2H}{C}}-CH_2-\overset{CH_3}{\underset{CO_2H}{C}}-$	Pt	γ-Lactone formation  (35–40) Methyl ester formation  (30) $-CH_2-\overset{CH_3}{\underset{CO_2CH_3}{C}}-CH_2-\overset{CH_3}{\underset{OH}{C}}-CH_2-$	726

TABLE XVI (*Continued*)

Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
Polymethacrylic acid (CH_3OH, $NaOCH_3$)	Pt	Olefin formation  $-CH_2-C(CH_3)(CO_2H)-CH=C(CH_3)-CH_2-$ (5–6)	726
		(g)[i] Rearrangement, Esterification, Halogenation	
β-Phenylisovaleric acid			
(a) (C_2H_5OH)	...	Isobutylbenzene, 2-methyl-3-phenyl-1-propane, 1-phenyl-2-methyl-1-propene, *t*-butylbenzene, ethyl phenylisovalerate, 2,2-dimethyl-2,2-diphenylhexane, neophyl 3-phenylisovalerate	798
(b) (CH_3OH, NaOAc)	Pt	*t*-Amylbenzene (32), 2,5-dimethyl-2,5-diphenylhexane (low), α,β-dimethylstyrene?	72
γ-Benzyl-γ-hydroxyvaleric acid (CH_3OH, $(C_2H_5)_3N$)	C	Isopropyl benzyl ketone (5), 1-phenyl-2-methylbutan-3-one (11), methyl benzyl ketone (80), ethylene	131
1-Hydroxycyclohexylacetic acid (CH_3CN, $(C_2H_5)_3N$	Pt	Cycloheptanone (45–53)	131
1-Hydroxycyclopentylacetic acid (CH_3CN, $(C_2H_5)_3N$)	Pt	Cyclohexanone (54–63)	131
1-Hydroxycycloheptylacetic acid (CH_3CN, $(C_2H_5)_3N$)	Pt	Cyclooctanone	131
Iodoacetic acid (H_2O, Na_2CO_3)	Pt	CH_2I_2, CO, CO_2, I_2, HI	403
Bromoacetic acid (H_2O, Na_2CO_3)	Pt	CH_2Br_2, CO, CO_2, Br_2, HBr	403
Chloroacetic acid (H_2O, Na_2CO_3)	Pt	CH_2Cl_2, chloromethyl chloroacetate, CO, CO_2, Cl_2, HCl, HCHO	403
Difluorochloroacetic acid	...	CF_2Cl_2, CO_2, Cl_2	748
Dichloroacetic acid (H_2O, Na_2CO_3)	Pt	Dichloromethyl dichloroacetate, CO_2, CO	403
Potassium α-bromopropionate (H_2O)	Pt	1,1-Dibromoethane (<10), Br_2	780
α-Bromovaleric acid			
(a) (CH_3OH, KOH)	Pt	Methyl α-bromovalerate (30), Br_2, methyl valerate (51)[h]	852
(b) (H_2O, KOH)	Pt	*n*-Butylbromide (25), 1,1-dibromobutane (27), *n*-octane (17),[h] Br_2	852
α-Bromocaproic acid			
(a) (CH_3OH, KOH)	Pt	Methyl α-bromocaproate (34), Br_2, methyl caproate (46)[h]	852
(b) (H_2O, KOH)	Pt	*n*-Pentylbromide (32), 1,1-dibromopentane (27), *n*-decane (14),[h] Br_2	852
α-Bromodiethylacetic acid			
(a) (CH_3OH, KOH)	Pt	Methyl α-bromodiethylacetate (15), Br_2, methyl diethylacetate (61)[h]	852
(b) (H_2O, KOH)	Pt	3-Pentanone (32), 2-bromo-3-pentanone (29), 2,4-dibromo-3-pentanone (trace), Br_2	852
α-Bromoisobutyric acid			
(a) (CH_3OH, KOH)	Pt	Methyl α-bromoisobutyrate (28), Br_2, methyl isobutyrate (53)[h]	852
(b) (H_2O, KOH)	Pt	Acetone (trace), bromoacetone (31), 1,1-dibromoacetone (19), 1,3-dibromoacetone (5), isobutyl bromide (trace), Br_2	852
Sodium α,α-dichloropropionate (H_2O)	...	α,α-Dichloroethyl α,α-dichloropropionate	462
11-Bromoundecanoic acid (CH_3OH, $NaOCH_3$)			
(a) (50°)	Pt	1,20-Dibromoeicosane (64)	850
(b) (65°)	Pt	Methyl 11-bromoundecanoate (71), methyl 11-methoxyundecanoate (2.4)	850

[a] Diaphragm. [b] No diaphragm. [c] Distribution of olefins, 5:6:3, respectively. [d] No *trans*-3-methyl-3-hexene present. [e] Products of hydrogenation. [f] Epimer of 20-ξ-methoxy-5α-pregnan-3β-ol. [g] The acetate could not be isolated because of its extreme ease of hydrolysis. [h] Cathodic product. [i] See also ref 851.

$$CH_3NHNHCH_3 \rightarrow CH_3N{=}NCH_3 + 2H^+ + 2e \quad \text{(Eq 123)}$$

$$CH_3N{=}NCH_3 \rightarrow CH_3NHN{=}CH_2 \quad \text{(Eq 124)}$$

$$CH_3NHH{=}CH_2 + H_2O \rightarrow CH_3NHNH_2 + HCHO \quad \text{(Eq 125)}$$

$$CH_3NHNH_2 + H_2O \rightarrow CH_3OH + N_2 + 4H^+ + 4e \quad \text{(Eq 126)}$$

Electrolysis of 9-hydrazoacridine in CH_3CN solution containing base gives the radical $RNH\dot{N}R$ (R is acridinyl) (92). Cpe at a potential between the half-wave potentials of the mono- and diprotonated forms affords an almost quantitative yield of diprotonated 9-azoacridine.

The anodic reaction of isonicotinoylhydrazine is pH dependent (508). At pH 11.2, cpe gives 1,2-diisonicotinoylhydrazine (**160**) and a small quantity of pyridine-4-aldehyde (**161**) in a two-electron oxidation. At the higher pH, isonicotinic acid (**159**) and **160** are formed. The reaction scheme in alkaline solution involving the oxidation of the anion **158** has been formulated according to Eq 127–131. In the more alkaline solution, **158** is less favored in the competition with hydroxyl ions for the isonicotinoyl cation, resulting in an increased yield of isonicotinic acid.

$$\underset{\mathbf{158}}{NC_5H_4CON_2H_2^-} + 2OH^- \rightarrow NC_5H_4CON{=}N^- + 2H_2O + 2e \quad \text{(Eq 127)}$$

$$NC_5H_4CON{=}N^- \rightarrow NC_5H_4CO^+ + N_2 + 2e \quad \text{(Eq 128)}$$

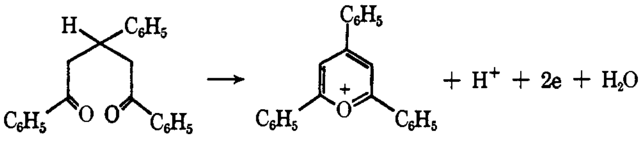
$$NC_5H_4CO^+ + OH^- \rightarrow \underset{\mathbf{159}}{NC_5H_4CO_2H} \quad \text{(Eq 129)}$$

$$NC_5H_4CO^+ + \mathbf{158} \rightarrow \underset{\mathbf{160}}{(NC_5H_4CONH\!-)_2} \quad \text{(Eq 130)}$$

$$NC_5H_4CON{=}N^- + H_2O \rightarrow \underset{\mathbf{161}}{NC_5H_4CHO} + OH^- + N_2 \quad \text{(Eq 131)}$$

The course of anodic oxidation of aldehydes and ketones generally follows the routes observed in chemical oxidation. The electrooxidation of furfural (or of furoic acid) at PbO_2 leads to β-formylacrylic acid and maleic acid. These products appear to result from 1,4 addition of hydroxy groups across the conjugated system (347).

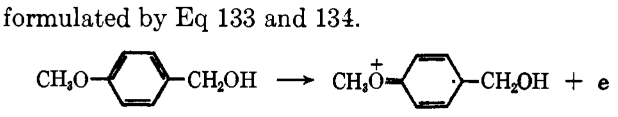
The oxidation of 1,3,5-triphenyl-1,5-pentanedione (**162**) in CH_3CN solution (71) gives 2,4,6-triphenylpyrylium perchlorate (**163**) in a process which appears to be analogous to the hydride-transfer reactions of 1,5-diketones observed with reagents such as triphenylmethyl perchlorate, ferric chloride, stannic chloride, polyphosphoric acid, or sulfuric acid in acetic anhydride (Eq 132) (11, 150, 719).



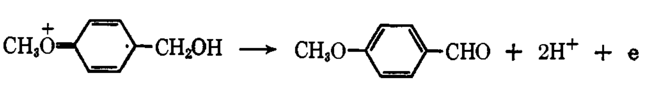
162 **163** (Eq 132)

Depending on reaction conditions, alcohols have been oxidized to a variety of products including aldehydes, ketones, amidine salts, carboxylic acids, monoalkyl carbonates, amides, trialkyl phosphates, and haloforms, etc. The mechanisms of oxidation of the simpler alcohols in aqueous media have been studied by a multitude of workers, often in connection with fuel-cell reactions.

Cpe of anisyl alcohol (**164**) in CH_3CN gives a good yield of anisaldehyde (**165**) provided that pyridine is present to act as a proton acceptor (510). The oxidation occurs in a two-electron process which may be formulated by Eq 133 and 134.

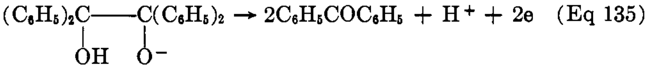


164 (Eq 133)



165 (Eq 134)

Ethylene glycol is successfully oxidized in stages at a Raney nickel anode in basic solution to glycolic acid or further to oxalic acid (715). The operating potential in this cpe is kept considerably below the reversible oxygen potential. In contrast benzopinacol and fluorenopinacol are oxidized in basic solution to benzophenone and fluorenone, respectively (324, 413). The central bond cleavage is facilitated by the relatively large carbon–carbon interatomic distance imparted by the bulky aromatic groups in the pinacolate anion **166** (Eq 135).

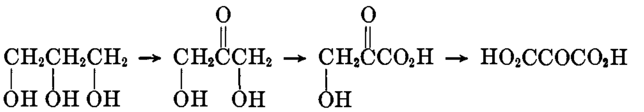


$$\underset{\substack{| \\ OH}}{(C_6H_5)_2C}\!\!-\!\!\!-\!\!\!-\!\!\underset{\substack{| \\ O^-}}{C(C_6H_5)_2} \rightarrow 2C_6H_5COC_6H_5 + H^+ + 2e \quad \text{(Eq 135)}$$

166

Anodic oxidation constitutes an excellent method of oxidizing sulfides to sulfoxides or to sulfones in high yield. In other reactions, sulfides or disulfides may be converted to sulfonic acids, and dithiocarbamate, mercaptide, trithiocarbonate, or xanthogenate salts to the corresponding disulfide derivative. The electrolysis of potassium thiostearate in CH_3OH in the presence of an excess of thiostearic acid gives a mixture of products consisting of distearoyl disulfide, methyl stearate, and a small amount of stearic acid. No hydrocarbons are formed in this reaction which has been depicted as involving discharge of the carbothiolate anion ($RCOS^-$) to give the acylthio radical ($RCOS\cdot$) in analogy with the Kolbe reaction (352). Dimerization of the latter accounts for formation of the disulfide, while methyl stearate is believed to result from a following chemical side reaction.

Cpe of glycerol at a Raney nickel electrode gives dihydroxyacetone, hydroxypyruvic acid, or mesoxalic acid (Eq 136) depending on the potential (715).



$$\underset{\substack{| \quad | \quad | \\ OH\;OH\;OH}}{CH_2CH_2CH_2} \rightarrow \underset{\substack{| \quad\;\; | \\ OH\;\;OH}}{CH_2\overset{\substack{O \\ \|}}{C}CH_2} \rightarrow \underset{\substack{| \\ OH}}{CH_2}\overset{\substack{O \\ \|}}{C}CO_2H \rightarrow HO_2CCOCO_2H \quad \text{(Eq 136)}$$

Aldoses (RxCHOHCHO) may be oxidized electrochemically to the corresponding aldonic acid ($RxCHOHCO_2H$) and the latter to the next lower aldose (RxCHO) with loss of carbon dioxide and water. With bromide electrolyte the oxidation is believed to occur *via* anodically generated hypobromite. Methyl glucoside has been *cathodically oxidized* to glucuronic acid by cathodically generated hydrogen peroxide (reduction of oxygen) (484).

Alloxan (**170**) is the main product of chemical oxidation of uric acid (**167**) under strongly acidic conditions; under less acidic conditions allantoin (**169**) is formed (55, 70). Recently, Struck and Elving (743) found that cpe of **167** at graphite in dilute acetic acid occurs in a two-electron process to give 0.25 mole of CO_2, 0.25 mole of a precursor of allantoin, 0.75 mole of urea, 0.3 mole of parabanic acid (**171**), and 0.3 mole of alloxan (**170**) per mole of uric acid. Their results indicate that an unstable intermediate (Eq 137) which may be a

TABLE XVII

MISCELLANEOUS OXIDATIONS

Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
Hydrazines, Hydrazides, Pyrazolones, and Related Compounds			
Methylhydrazine (H_2O, H_2SO_4), cpe 1.0 V *vs.* sce	Pt	CH_3OH, N_2 (quant)	418
1,2-Dimethylhydrazine (H_2O, H_2SO_4), cpe 1.0 V *vs.* sce	Pt	CH_3OH, HCHO, N_2 (104)	418
1,1-Dimethylhydrazine (H_2O, H_2SO_4), cpe 1.0 V *vs.* sce	Pt	CH_3OH, HCHO (80), N_2 (83), $(CH_3)_2NH$	418
Hydrazobenzene			
(a) (Liq NH_3, NH_4Cl)	Pt	Azobenzene (80)	120, 317
(b) (CH_3CN, C_5H_5N, $NaClO_4$)	Pt	Azobenzene (10.8), polymer	820
4,4'-Dimethoxyazobenzene (CH_3CN, C_5H_5N, $NaClO_4$)	Pt	Polymer	820
4,4'-Dimethylazobenzene (CH_3CN, C_5H_5N, $NaClO_4$)	Pt	Polymer	820
4,4'-Dichlorohydrazobenzene (CH_3CN, C_5H_5N, $NaClO_4$)	Pt	4,4'-Dichloroazobenzene (82)	820
9-Hydrazoacridine			
(a) (CH_3CN, $LiClO_4$, diphenylguanidine), cpe 0.300 V *vs.* Ag, Ag^+ (0.01 *M*)	Hg	$RNH\dot{N}R$[a]	92
(b) (CH_3CN, $LiClO_4$, acid), cpe 0.900 V *vs.* Ag, Ag^+ (0.01 *M*)	Hg	9-Azoacridinium diperchlorate (98)	92
1-Isonicotinoyl-2-phenylhydrazine (H_2O, pH 11.9), cpe 0.00 V *vs.* sce	Hg	Isonicotinic acid (90), aniline (trace), N_2	508
Isonicotinoyl hydrazide			
(a) (H_2O, pH 11.2), cpe 0.00 V *vs.* sce	Hg	1,2-Diisonicotinoylhydrazine (80), pyridine-4-aldehyde (5)	508
(b) (H_2O, pH 13), cpe 0.00 V *vs.* sce	Hg	Isonicotinic acid (45), 1,2-diisonicotinoylhydrazine (55)	508
5-Nitro-2-furfural thiosemicarbazone (H_2O, $KFe(SO_4)_2$)	Pt	2-(5-Nitro-2-furyl)-5-amino-1,3,4-thiadiazole (65)	10, 682
1,5-Diphenylthiocarbazide (H_2O, acetone, KOH), cpe −0.2 V *vs.* sce	Pt	Dithizone (88.9)	597
Diphenylpicrylhydrazyl (CH_3CN, $NaClO_4$)[b]	Pt	Corresponding cation	292, 334, 737
1-Phenyl-3-methylpyrazolone (H_2O, H_2SO_4)	Pt	Methylene diphenylmethylpyrazolone, bis-1-phenyl-3-methyl-5-pyrazolone (10)	216, 824
1-Phenyl-2,3-dimethylpyrazolone (H_2O, H_2SO_4)	Pt	Decomposition products	216
1-Phenyl-3,4-dimethylpyrazolone (H_2O, H_2SO_4)	Pt	Bis-1-phenyl-3,4-dimethyl-5-pyrazolone (5), fumaric acid	216
1-Phenyl-3-methyl-4-ketopyrazolone (H_2O, H_2SO_4)	Pt	Decomposition products	216
4-Amino-1-phenyl-3-methylpyrazolone (H_2O, H_2SO_4)	PbO_2	Rubazonic acid	216
Carbonyl Functions			
Acetaldehyde			
(a) (H_2O, O_2)	C, Pt	Peracetic acid, HOAc	513, 859
(b) (H_2O, H_2SO_4)	Pt	Acetic acid, CO_2, CH_4, CO	101, 125, 346, 470
Acrolein (H_2O, H_2SO_4)	Pt	Acrylic acid	471
Propionaldehyde (H_2O, H_2SO_4)	Pt	Propionic acid	458, 470
Isobutyraldehyde (H_2O, H_2SO_4)	Pt	Isobutyric acid CO, CO_2	470
Furfural (H_2O, H_2SO_4)	PbO_2	β-Formylacrylic acid, maleic acid, succinic acid, malic acid	144, 347, 859
Furoic acid (H_2O, H_2SO_4)	PbO_2	β-Formylacrylic acid, maleic acid	347
Benzaldehyde (H_2O, sodium benzenesulfonate, CuO)	Pt, Ni	Benzoic acid (58)	471, 531
Anisaldehyde (H_2O, H_2SO_4)	Pt	Anisic acid (95)	242
Acetone			
(a) (H_2O, acid or base)	Pt, Fe, Ni	HOAc, HCO_2H, CO_2, CO, C_2H_6	424, 712
(b) (H_2O, HCl)	C, Pt	Chloroacetone (97)	664, 665, 712, 751
(c) (H_2O, HBr)	Pt	Bromoacetone	664
(d) (H_2O, base)[c]	Hg	CH_3COCH_2HgOH	351
(e) (H_2O, KCl)	Pt	Chloroform (quant)	65, 203, 712, 776, 816
(f) (H_2O, KBr)	Pt	Bromoform (quant)	136, 572
(g) (H_2O, KI)	Pt	Iodoform (90–95)	2, 175, 681, 775
Methyl ethyl ketone (H_2O, KCl)	Pt	Chloroform (47), HOAc	203
Cyclohexanone			
(a) (H_2O, H_2SO_4)	PbO_2, Pt	Adipic acid, tartaric acid, malonic acid, CO_2, CO; maleic acid, condensation products	634, 862

TABLE XVII (*Continued*)

Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
(b) (H_2O, HCl)	C	α-Chlorocyclohexanone	751
Acetophenone			
(a) (H_2O, H_2SO_4)	PbO_2	Fumaric acid, maleic acid	745
(b) (H_2O, HCl, HOAc)	C	α-Chloroacetophenone (80)	751
Propiophenone (H_2O, HOAc, HCl)	Pt	α-Chloropropiophenone, β-chloropropiophenone	751
Benzil (H_2O, acetone, H_2SO_4)	Pt	Benzoic acid (7.6 g/10 gsm)	387, 471
Benzoin ethyl ether (H_2O, acetone, H_2SO_4)	Pt	Benzaldehyde (2.2 g/10 gsm), benzoic acid (3.2 g)	471
Benzoin acetate (H_2O, acetone, H_2SO_4)	Pt	Benzaldehyde (2.2 g/10 gsm), benzoic acid (1.3 g)	471
Benzophenone (H_2O, HOAc, HCl)	C	Monochlorobenzophenone (70)	751
1,3,5-Triphenyl-1,5-pentanedione (CH_3CN, $LiClO_4$)	Pt	2,4,6-Triphenylpyrylium perchlorate	71
4-Methyl-3,5-heptadien-2-one (CH_3CN, $LiClO_4$)	Pt	No pyrylium salt formed	71
2-Methylbenzoquinone (H_2O, H_2SO_4)	PbO_2	Mesaconic acid, maleic acid, racemic acid, HCO_2H, CO_2, CO	863
Butyrolactone (H_2O, H_2SO_4)	PbO_2	Succinic acid (quant)	381
Acetic anhydride (HOAc, $NaClO_4$)	Pt[j]	Acetylium ion, H^+	523
Diethyl carbonate			
(a) (CH_3CN, KI, I_2)	Pt	CH_4, CO_2, H_2, CO, C_2H_6, C_2H_5OH, ethyl acetate, ethyl cyanoacetate, diethyl oxalate	602
(b) (Tetrahydrofuran, CH_3CN, KI, I_2)	Pt	α-Carbethoxytetrahydrofuran	602
		Alcohols and Glycols	
Methanol			
(a) (H_2O, H_2SO_4)	Pt, PbO_2	HCHO, HCO_2H, CO, CO_2, methylsulfonic acid, methylal	152, 173, 485, 663
(b) (H_2O, NaOH)	Pt	HCHO, HCO_2Na	440, 571, 573, 618, 773
(c) ($NaOCH_3$)	Pt	Sodium monomethyl carbonate,[k] CO	689, 690, 750
(d) ($NaOCH_3$)	Pb	Lead methoxide, lead dimethyl carbonate[k]	750
(e) (KOAc)	Pt	Potassium monomethyl carbonate, C_2H_6	332
(f) (NH_3, NH_4NO_3)	Pt	Urea	264, 265
(g) (P, HCl (gas))	C	Trimethyl phosphate (77.5), methyl chloride	803
Ethanol			
(a) (H_2O, NaCl)	Pt	Chloroform (quant)	97, 203, 697, 786
(b) (H_2O, NaBr, $CaBr_2$)	Pt	Bromoform	175, 481
(c) (H_2O, KI)	Pt	Iodoform (97.7)	97, 153, 175, 270, 284, 411, 476, 712, 815
(d) (H_2O, NaOH)	Pt	CH_4, CO_2	440, 573
(e) (KOAc)	Pt	Potassium monoethyl carbonate	332
(f) ($NaOC_2H_5$)	Pt	Sodium monoethyl carbonate	750
(g) ($NaOC_2H_5$)	Mg	Magnesium ethoxide, magnesium diethyl carbonate[k]	750
(h) ($(NH_4)_2CO_3$)	Pt	Acetamidine nitrate	264, 265
(i) (HCl, KCl)	C	Chloral (51.3)	98, 311
(j) (H_2O, H_2SO_4)	Pt, PbO_2	Acetaldehyde, HOAc, ethylsulfonic acid, ethyl acetate, CO_2	20, 40, 152, 173, 328, 386, 532, 660, 698, 849, 857, 858
(k) (P, HCl (gas))	C	Triethyl phosphate (55)	803
n-Propyl alcohol			
(a) (H_2O, H_2SO_4)	Pt, PbO_2	Propionaldehyde, propionic acid, CO, CO_2	173, 189, 660, 712
(b) (H_2O, NaOH)	Pt	C_2H_4, CH_4, C_2H_6, CO_2	439, 458, 570
(c) (H_2O, $(NH_4)_2CO_3$)	Pt	Propionamidine nitrate	266
(d) (H_2O, $CaCl_2$)	Pt	Chloroform	203
Isopropyl alcohol (H_2O, H_2SO_4)	Pt	Acetone (70), HOAc, HCO_2H, CO_2	173, 458
n-Butyl alcohol			
(a) (H_2O, H_2SO_4)	Pt	Butyric acid, butyl butyrate	189, 651, 652
(b) (H_2O, $(NH_4)_2CO_3$)	Pt	Butyramidine nitrate	266
(c) (P, HCl (gas))	C	Tri-*n*-butyl phosphate (88.3)	803
Isobutyl alcohol (H_2O, H_2SO_4)	PbO_2	Isobutyric acid (60)	30, 189, 273
Amyl alcohol (P, HCl (gas))	C	Triamyl phosphate (63.1)	803
Isoamyl alcohol (H_2O, H_2SO_4)	PbO_2	Isovaleraldehyde, isovaleric acid (80)	173, 189, 438
n-Hexanol (H_2O, H_2SO_4)	PbO_2	Caproic acid (16.7), *n*-hexyl caproate (16.7), CO_2 (5.6), CO	505
Cyclohexanol (H_2O, Na_2CO_3)	Pt, PbO_2	Cyclohexanone, maleic acid, butyric acid	207, 261, 862
Borneol or isoborneol (H_2O, HNO_3)[d]	Mn, Cr	Camphor	21, 305, 735

TABLE XVII (*Continued*)

Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
Menthol (H_2O, H_2SO_4)[d]	...	Menthone	468
Tropine or pseudotropine (H_2O, H_2SO_4)	PbO_2	Tropinone	542, 543
Tetrahydrofurfuryl alcohol (H_2O, H_2SO_4)	PbO_2	Succinic acid (good)	763
Benzyl alcohol (H_2O, Na_2CO_3)	Pt, Ni	Benzaldehyde, benzoic acid	439, 531
Anisyl alcohol (CH_3CN, C_5H_5N, $NaClO_4$), cpe 1.35 V *vs.* Ag, Ag^+ (0.1 *N*)	Pt	Anisaldehyde[e] (72)	510
1,2,3,4-Tetrahydro-1-naphthol (*t*-BuOH, H_2O, NaOH, cyclohexyltrimethylammonium hydroxide)	Pt	α-Tetralone (50)	395
Propargyl alcohol (H_2O, H_2SO_4)	Cu, PbO_2	Propiolic acid (76.1)	847, 848
Phenoxyethanol (strong acid)	...	Side-chain oxidation	22
Ethylene glycol			
(a) (H_2O, H_2SO_4)	PbO_2	Glycolaldehyde, glycolic acid, HCHO, HCO_2H	500, 586, 663
(b) (H_2O, KOH), cpe	Raney Ni	Glycolic acid	715
(c) (H_2O, KOH), cpe	Raney Ni	Oxalic acid	715
Glycolic acid	Pt	HCHO	589
Butynediol (H_2O, H_2SO_4)	PbO_2	Acetylenedicarboxylic acid (73.9)	327, 848
Hexan-2,4-diyne-1,6-diol (H_2O, H_2SO_4)	Cu, PbO_2	Diacetylenedicarboxylic acid dihydrate (8.2)	848
Benzopinacol (H_2O, NaOH)	Hg[c]	Benzophenone	413
Fluorenol (CH_3CN, C_5H_5N, $NaClO_4$), cpe	Pt	Insoluble tar	510
Fluorenopinacol (H_2O, C_2H_5OH, NaOH)	Hg[c]	Fluorenone	324
		Sulfur Functions	
Methyl sulfide (H_2O, CH_3OH, HCl)[b]	Pt	Dimethyl sulfoxide	591
Ethyl sulfide (HOAc, concd HCl)	Pt	Ethyl sulfoxide (70.5), ethyl sulfone	268, 591
Pentamethylene sulfide (H_2O, CH_3OH, HCl)[b]	Pt	Pentamethylene sulfoxide	591
2,2′-Dihydroxyethyl sulfide (H_2O, NaCl)	C, Pt	2,2′-Dihydroxyethyl sulfone (90)	649
Methyl phenyl sulfide (H_2O, CH_3OH, HCl)[b]	Pt	Methyl phenyl sulfoxide	591
Ethyl phenyl sulfide (HOAc, HCl)	Pt	Benzenesulfonic acid	268
Phenyl sulfide			
(a) (HOAc, H_2O, HCl)	Pt	Phenyl sulfoxide (82)	211, 252
(b) (HOAc, H_2O, HCl)	Pt	Phenyl sulfone (93)	211, 252
Benzyl sulfide			
(a) (HOAc, H_2O, HCl)	Pt	Benzyl sulfoxide (92.7)	252, 591
(b) (HOAc, H_2SO_4)	Pt	Tribenzyl sulfinium sulfate (90.8)	252
p-Nitrobenzyl sulfide (HOAc, cond HCl)	Pt	*p*-Nitrobenzyl sulfoxide (63)	268
o-Nitrobenzyl sulfide (HOAc, concd HCl)	Pt	*o*-Nitrobenzyl sulfoxide (93.4), *o*-nitrobenzyl disulfoxide (3.1)	268
Methionine (H_2O)	Pt	Dehydromethionine	518
Acetone ethyl thioacetal (HOAc, HCl)	C	Diethylthionyl-2,2-propane (1 g/4 gsm)	211, 268
$C_nH_{2n+1}SCH_3$ (H_2O, base)	...	$(C_nH_{2n+1})_2S_2$	593
Sodium ethyl mercaptide (C_2H_5OH)	...	Ethyl disulfide	82
Sodium phenyl mercaptide (C_2H_5OH)	...	Phenyl disulfide	82, 753
Methyl disulfide (H_2O, alkanesulfonic acid)	Pt	Methanesulfonic acid (37.8)	77
Ethyl disulfide (H_2O, ethanesulfonic acid)	Pt	Ethanesulfonic acid (80)[f]	77
Phenyl disulfide (HOAc, H_2O, HCl)	Pt	Benzenesulfonic acid	268
Ammonium phenyl disulfide 4,4′-disulfonate (H_2O)	Pt	*p*-Benzenedisulfonic acid (88)	210
Benzyl disulfide (HOAc, H_2SO_4)	Pt	Benzyl disulfoxide (92.7)	252
Dimethyl sulfoxide (H_2O, H_2SO_4)	PbO_2	Dimethyl sulfone (99)	268, 361
Potassium thioacetate (C_2H_5OH)	...	Diacetyl disulfide	81
Sulfone diacetic acid (H_2O)	Pt	H_2SO_4, CO_2	224
Thiostearic acid (CH_3OH, KOH)	Pt	Methyl stearate (>37), distearoyl disulfide (31), stearic acid (4)	352
Sodium thioglycollate (H_2O, acid, neutral, or alkaline pH)	Pt	Corresponding disulfide	619
Thiobenzamide (H_2O, C_2H_5OH, NaOH), cpe −0.35 V *vs.* sce	Hg	Benzonitrile, benzamide, HgS	509
Thiobenzanilide (H_2O, C_2H_5OH, NaOH), cpe −0.35 V *vs.* sce	Hg	$C_6H_5N{=}C(C_6H_5)SHgSC(C_6H_5){=}NC_6H_5$	509
Sodium diethyldithiocarbamate[a]	Hg, Pt	$[(C_2H_5)_2NC(S)S]_2$	326, 799
Diethylammonium diethyldithiocarbamate (H_2O)	Pt	Tetraethylthiuram disulfide	695
Ammonium dithiocarbamate (H_2O)	Pt	Thiuram disulfide	695
Potassium methylxanthogenate (H_2O)	Pt	Bismethylxanthogen	694, 695
Potassium ethylxanthogenate (H_2O)	Pt	Dixanthogen	693
Potassium isobutylxanthogenate (H_2O)	Pt	O-Isobutylthiocarbonic acid disulfide	694, 695
Potassium isoamylxanthogenate (H_2O)	Pt	O-Isoamylthiocarbonic acid disulfide	694, 695
Potassium ethyl trithiocarbonate (H_2O)	Pt	Ethyl trithiocarbonic acid disulfide	695
Potassium phenylsulfocarbazinate	...	Diphenyl thiocarbazide	695
Ethyl thiocyanate (HOAc, Ac_2O, HCl)	Pt	Ethylsulfonic acid	268
Potassium methylsulfonate (H_2O)	Pt	HCHO, CO_2, H_2SO_4	226
Trichloromethylsulfonic acid (H_2O)	Pt	CO_2, HCl, H_2SO_4	443
Methyldisulfonic acid (H_2O)	Pt	CO_2, H_2SO_4	226

TABLE XVII (*Continued*)

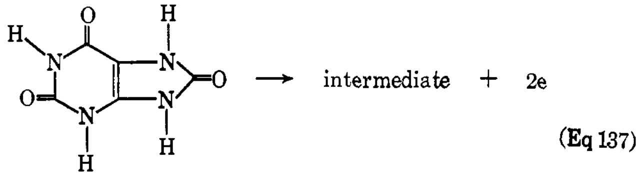
Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
Benzenesulfonic acid (H_2O)	Pt, PbO_2	*p*-Hydroxybenzenesulfonic acid, benzoquinone, fumaric acid, succinic acid, 3,4-dihydroxybenzenesulfonic acid	262, 784a
Potassium benzenesulfonate (H_2O, KCl)	Pt	Trichlorobenzoquinone, tetrachlorobenzoquinone, *m*-chlorobenzenesulfonic acid, 3,5-dichlorobenzenesulfonic acid, 3,4,5-trichlorobenzenesulfonic acid	365
o-Toluenesulfonic acid (H_2O)	Pt, PbO_2	2-Carboxy-4,5-dihydroxybenzenesulfonic acid, mesaconic acid	262
p-Toluenesulfonic acid (H_2O, H_2SO_4)	PbO_2	*p*-Sulfobenzoic acid (30)	707
Sodium α-naphthalenesulfonic acid (H_2O)	Pt	Phthalic acid	142
Ammonium *m*-benzenedisulfonate (H_2O)	Pt	Phenol-2,4-disulfonic acid, benzoquinone, 3,4-dihydroxybenzenesulfonic acid	210
p-Benzenedisulfonic acid (H_2O)	Pt, PbO_2	Phenol-2,5-disulfonic acid, 3,4-dihydroxybenzenesulfonic acid, fumaric acid	210, 262
Phenol-2,4-disulfonic acid (H_2O, H_2SO_4)	Pt	3,4-Dihydroxybenzenesulfonic acid, benzoquinone	210
Phenol-2,5-disulfonic acid (H_2O, H_2SO_4)	Pt	CO_2, H_2SO_4	210
Sugars, Polyols, and Related Compounds			
Glucose			
(a) (H_2O, NaBr, $CaCO_3$)	Fe, Ni, C, Cu, Pb	Calcium gluconate (85–100), calcium 5-ketogluconate (10)	69, 128, 271, 375, 377, 380, 674, 675, 752
(b) (H_2O, H_2SO_4)	PbO_2	Gluconic acid, arabinic acid, arabonic acid, trihydroxyglutaric acid, saccharic acid, HCHO, HCO_2H, CO_2	498, 499, 662
d-Galactose (H_2O, KBr, $CaCO_3$)	C	Calcium galactonate (60–70)	271, 377, 415
3-Methylglucose (H_2O, $CaBr_2$, $CaCO_3$)	Pt	Calcium 3-methylgluconate (quant)	702
d-Mannose (H_2O, $CaBr_2$, $CaCO_3$)	C	Calcium mannonate (92.2)	45, 271, 416
d-Xylose			
(a) (H_2O, $CaBr_2$, $CaCO_3$, $CdBr_2$)	C	Cadmium xylonate (65)	271, 378
(b) (H_2O, Br^-, $MgCO_3$)	C	Magnesium xylonate (80)	378
(c) (H_2O, NaBr, $SrCO_3$)	C	Strontium xylonate (95)	355
d-Maltose (H_2O, KBr, $CaCO_3$)	C	Calcium maltobionate (74.4)	271, 377
d-Lactose (H_2O, KBr, $CaCO_3$)	C	Calcium lactobionate (73–90)	271, 330, 376, 377, 379
Mannitol	. . .	Polyoxymethylene, HCO_2H	663
Arabinose (H_2O, $CaBr_2$, $CaCO_3$)	Pt	Calcium arabinate (65–71.3)	271, 739
Methylglucoside (H_2O, H_2SO_4, Na_2SO_4, O_2), cpe <0.3 V *vs.* 1 *N* calomel electrode	Hg[i]	Glucuronic acid (20)	484
3,5-Benzylidene-1,2-cyclohexylidene-D-glucose (H_2O, $KMnO_4$, NaOH)	Cu	3,5-Benzylidene-1,2-cyclohexylidene-D-gluconic acid (53)	774
Di-O-isopropylidene-L-sorbose (H_2O, NO_3^-, NO_2^-, or Br^-)	Cu, Ni, Ag Monel	Di-O-isopropylidene-L-*xylo*-hexulosonic acid (70)	725, 807
Erythronic acid (H_2O, $CuCO_3$)	Pt	Glycerinaldehyde	588, 589
l-Arabonic acid (H_2O)	Pt	*l*-Erythrose	585
d-Gluconic acid (H_2O)	Pt	*d*-Arabinose	585
Saccharic acid (H_2O, H_2SO_4)	Pt	Tartaric acid dialdehyde, tartaric acid	149, 585
d-Galactonic acid (H_2O, $CuCO_3$)	Pt	*d*-Lyxose	589
Calcium *d*-gluconate (H_2O, HOAc, $CaBr_2$, CrO_3)	C	Calcium ketogluconate (80)	614
Sodium *l*-iodonate (H_2O, HOAc, NaBr, CrO_3)	C	Sodium ketoidonate (50)	614
Calcium 2-keto-D-gluconate (H_2O, $CaBr_2$, acid)	. . .	Calcium D-arabonate	535
Glycerol			
(a) (H_2O, H_2SO_4)	PbO_2	Acrolein, glycerinic acid, tartronic acid, pentose, $C_6H_{12}O_6$, HOAc, HCHO, HCO_2H, polyoxymethylene	34, 416, 500, 586
(b) (H_2O, KOH) cpe 0.145 V *vs.* rhe	Raney Ni	Dihydroxyacetone	715
(c) (H_2O, KOH) cpe 0.225 V *vs.* rhe	Raney Ni	Hydroxypyruvic acid	715
(d) (H_2O, KOH) cpe 0.385 V *vs.* rhe	Pd–C	Mesoxalic acid	715
Glycerinic acid (H_2O, $CuCO_3$)	Pt	Glycolaldehyde, CO_2, HCHO, HCO_2H	552, 585, 589
Malic acid	. . .	Malonic acid, oxalic acid, acetaldehyde	66, 552, 784
Tartronic acid (H_2O, base)	Cu	Mesoxalic acid, glyoxalic acid, oxalic acid, HCO_2H	770
Tartaric acid (H_2O, base)	Pt	Dihydroxymaleic acid, oxalic acid, mesoxalic acid, glyoxal, glyoxalic acid, tartronaldehydic acid, tartronic acid	585, 716–718
Other Functions			
Acetamidine (liq NH_3, KNH_2)	Pt	Cyanamide, C_2H_6, N_2	291
n-Valeramidine (liq NH_3, KNH_2)	Pt	Carbon deposit, C_2H_6, N_2	291
N-Nitrosopiperidine (H_2O, H_2SO_4)	Pt	$C_{10}H_{18}N_2$	7, 8
N-Nitroso-2-methylpiperidine (H_2O, H_2SO_4)	Pt	Norleucine, $C_{12}H_{24}N_2$	835
Uric acid			
(a) (H_2O, Li_2CO_3)	PbO_2	Allantoin (68.5), carbonyl diurea (13.8)	223

Table XVII (*Continued*)

Compound (solvent, electrolyte)	Anode	Product(s) (% yield)	Ref
(b) (Concd H_2SO_4)	PbO_2	Alloxan, parabanic acid, urea (62.9)	223
(c) (H_2O, HOAc, NaOAc), cpe 1.0 V *vs.* sce	C	CO_2 (25), allantoin (25), urea (75), parabanic acid (30), alloxan (30)	743
Ammonium carbonate			
(a) (liq NH_3)	C	Urea	204, 553
(b) (NH_4OH)	Pt	Urea	254
Potassium cyanide (H_2O, KOH)	Pt	Potassium cyanate	146, 615
Ammonium acetate (NH_4OH)	Pt	Urea	205, 227
Acetonitrile (perchlorate salt)	Pt	Succinonitrile, $HClO_4$	47, 445, 514, 701, 805
Cyclopentanone–sodium bisulfite adduct (H_2O)	Pt	γ-Valerolactone (17–20), δ-valerolactone	610
Cyclohexanone–sodium bisulfite adduct			
(a) (H_2O)	Pt	4-Hydroxyhexanoic acid lactone (17–20), 5-hydroxyhexanoic acid lactone	610
(b) (CH_3OH)	Pt	Methyl 5-methoxyhexanoate	610
Diethyl ether (H_2O, $HClO_4$)	Pt	Acetaldehyde (30)	522
Tetrahydrofuran (H_2O, H_2SO_4)	PbO_2	Succinic acid	75
3β-Cholestanol acetate (H_2O, HOAc, NaOAc)	Au, Pt	3-Acetoxyetioallocholanone[g]	448
3β-Epicholestanol acetate (HOAc, NaOAc)	Au, Pt	Androsterone[g]	448
Cholesteryl acetate dibromide (HOAc, NaOAc)	Pt	Dehydroandrosterone[g,h]	448
Cacodylic acid (H_2O, NaOH)	Pt	Monomethylarsenic acid, arsenic acid	217
Selenophenol (C_2H_5OH, base)	...	Phenyl diselenide	753

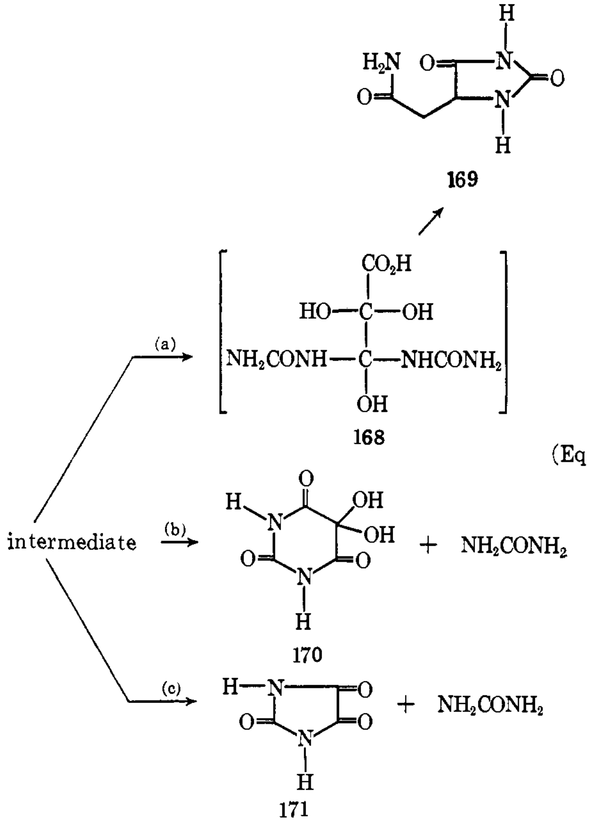
[a] R = 9-acridinyl. [b] Voltammetric study. [c] Polarographic study. [d] Inorganic "oxygen carrier" present. [e] Isolated as 2,4-dinitrophenylhydrazone. [f] Current efficiency. [g] Isolated as the semicarbazone. [h] Product of chemical reduction. [i] Cathodic oxidation by electrochemically generated hydrogen peroxide. [j] Chronopotentiometric study. [k] High current density required.

dicarbonium ion undergoes three simultaneous transformations: hydrolysis to an allantoin precursor (perhaps **168**) (Eq 138a); hydrolysis to alloxan **170** and urea (Eq 138b); oxidation and hydrolysis to parabanic acid and urea (Eq 138c). The electrochemical oxidation more nearly resembles the enzymatic oxidation (617, 733) than the chemical oxidation.



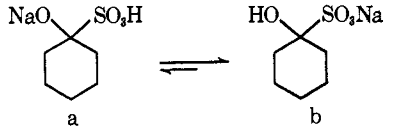
167

(Eq 137)



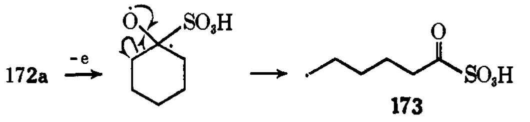
(Eq 138)

An interesting method of electrochemical synthesis of γ- and δ-lactones by oxidation of sodium bisulfite addition products of cycloalkanones has been reported (610). Thus electrolysis of the cyclohexanone–sodium bisulfite addition product (**172**) in aqueous solution affords a mixture of 4-hydroxyhexanoic acid lactone (**175**) and 5-hydroxyhexanoic acid lactone (**176**) in a ratio of 3:2. Since the acid-catalyzed reaction (155, 492) of 5-hexenoic acid gives the same relative amounts of **175** and

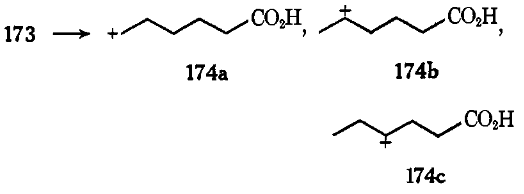


172

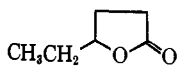
(Eq 139)



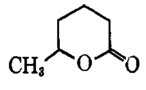
(Eq 140)



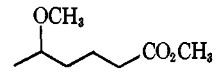
(Eq 141)



175



176



177

176, an electrochemical mechanism has been suggested involving discharge of the alkoxide **172a** followed by a subsequent ring-opening reaction to the radical **173** which is further oxidized to a mixture of carbonium ions **174a–c**. The relative stabilities of **174a–c** account for the products. Electrolysis of **172** in CH_3OH gives methyl 5-methoxyhexanoate (**177**) as the major product which is consistent with the existence of the carbonium ion **174b** during the reaction.

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